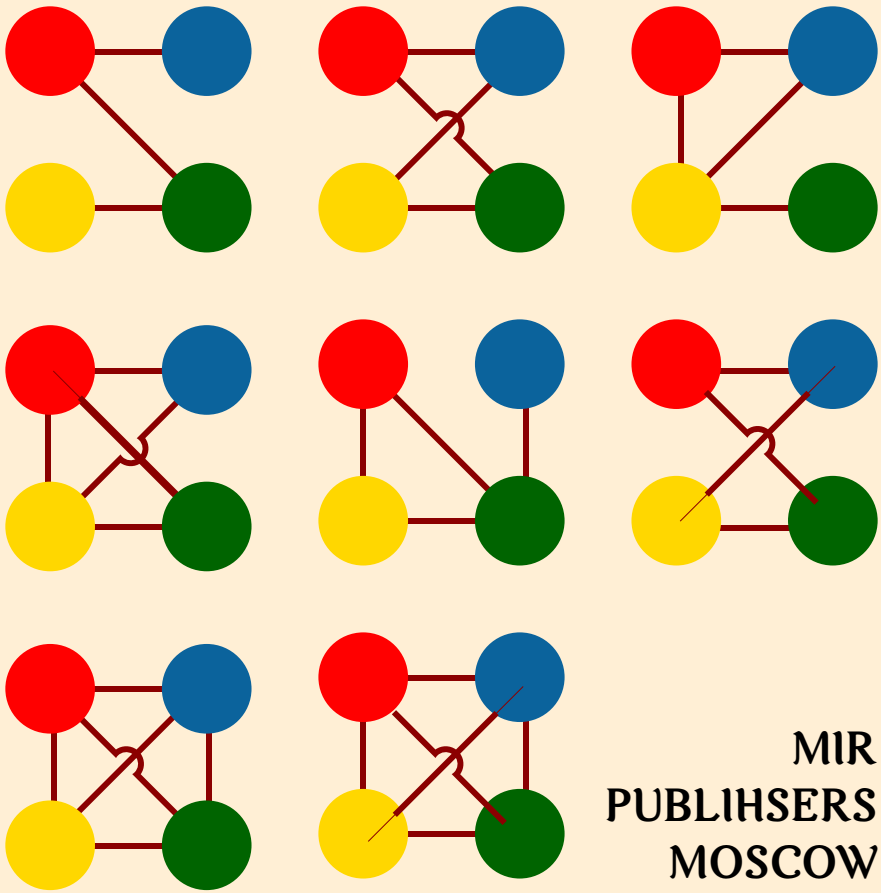
Thermodynamics, Statistical Physics, and Kinetics

Yu. B. Rumer, M. Sh. Ryvkin



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ТЕРМОДИНАМИКА, СТАТИСТИЧЕСКАЯ ФИЗИКА И КИНЕТИКА

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PREFACE

This book is intended for readers taking up the study of thermodynamics, statistical physics and kinetics. Accordingly, readers are assumed to have a knowledge of elementary physics, higher mathematics and quantum mechanics.

The sections marked by asterisks require a deeper knowledge and can be omitted on the first reading.

The book aims to gradually familiarize readers with methods used in thermodynamics, statistical physics and kinetics, to show how the concrete problems should be solved and to bring readers as soon as possible to a level which enables them to tackle more specialized books and papers. It has therefore proved necessary to include some matter, perhaps too simple for some, as well as problems that may be too difficult for others.

It was the desire to cover as quickly as possible the introductory stages and pass to concrete problems that dictated to a great extent the methods followed by the authors in introducing basic concepts. For instance, in the part of the book devoted to phenomenological thermodynamics the concepts of entropy and temperature are introduced simultaneously early on, an extensive use of Jacobians then allowing us to offer an integrated approach to solving problems for a wide range of monovariant (and later on polyvariant) thermodynamic systems. For the same reason we begin the treatment of the fundamentals of statistical physics by outlining the "cells and boxes" method, which although only suitable for ideal gases, does provide a simple solution to a wide range of problems. The more general Gibbs ensemble method is introduced later.

We would like to place special emphasis on the following. The treatment of the fundamentals of statistical physics begins with a discussion of the hypothesis of the indistinguishability of particles, without this being linked to any quantum-mechanical ideas. We wished to underline, thereby, the fact that along with the two methods historically used to uncover the wave nature of matter—matrix mechanics, based on the correspondence principle (Heisenberg-Bohr) and wave mechanics, based on the optical-mechanical analogy (Schrödinger-Hamilton)—a third way, obviously that used by A. Einstein, is possible, based on statistical mechanics. Our belief in the existence of this method derives from the fact that in the statistics of indistinguishable objects the volume of an elementary cell in the phase volume is not arbitrary, but is predetermined unambiguously by natural laws. This is why, in principle,

this method should be experimentally discoverable, and Planck's constant could appear in physics not as a result of an analysis of radiation laws (M. Planck) or photoeffect laws (A. Einstein), but from, for instance, the measurement of the heat capacity of an electron gas at low temperatures.

For this reason we use Planck's constant h, appearing naturally in statistical physics as a measure of the phase volume, and not the constant $\hbar$, more suitable in quantum mechanics.

Most sections of the book contain problems. We found it inexpedient to give solutions to the problems, not simply for reasons of space, but also in the belief that the independent solution of problems is far more beneficial than the study of provided solutions. Thus usually only answers are given to the problems, with brief hints given in some cases.

In conclusion, we wish to extend thanks to G. L. Kotkin, G. G. Mikhailichenko, V. G. Zelevinskii and V. S. L'vov for their great assistance in writing this book.

Yu. B. Rumer, M. Sh. Ryvkin

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INTRODUCTION

Thermodynamics, statistical physics and kinetics are concerned with the physical processes occurring in macroscopic systems, i.e. in bodies containing an enormous number of microparticles (atoms, molecules, ions, electrons, photons, etc. depending on the kind of the system).

There are two methods of studying the states of macroscopic systems—the *thermodynamic* and the *statistical method*. The *thermodynamic method* is independent of any models of the atomic and molecular structure of matter and is essentially a phenomenological method, meaning that its object is to establish relationships between directly observed (that is measured in macroscopic tests) quantities, such as pressure, volume, temperature, concentration of a solution, intensity of an electric or magnetic field and luminous flux. Quantities associated with the atomic and molecular structure of matter (dimensions of an atom or a molecule, their masses, number, etc.) are not used by the thermodynamic method in the solving of problems.

In contrast to this, the *statistical method* of studying the properties of macroscopic bodies is based from the outset on atomic-molecular models. The main object of statistical physics can thus be formulated as follows: using the laws governing the behaviour of the particles of a particular system (molecules, atoms, ions, quanta, etc.) to establish the laws governing the behaviour of macroscopic quantities of substance.

It is implied in all this that both the thermodynamic and statistical approaches have their merits and shortcomings in studying various phenomena.

The thermodynamic method, being independent of conceptual models, is characterized by a rather high degree of generality, while the results obtained from the use of statistical physics are true only to the extent that the assumptions made concerning the behaviour of the smallest particles of a system are valid.

The thermodynamic method is distinguished, as a rule, by great simplicity and it opens the way, after a number of simple mathematical procedures, to the solution of a large number of specific problems, without any information on the properties of atoms or molecules being required. This is an invaluable advantage of the thermodynamic method, especially when solving practical problems of a technical character (engineering thermodynamics, heat engineering).

The thermodynamic method possesses, however, a fundamental shortcoming, in that with this method the internal (atomic and mo-

lecular) mechanism of the phenomena involved remains unknown.

For this reason in thermodynamics the question "Why?" is meaningless. If, for instance, the thermodynamic method is applied to establish that a copper wire cools upon rapid extension, while a rubber band becomes hot (this problem will be considered in Sec. 14), we must be satisfied with the simple fact, with the physical mechanism leading to this result remaining hidden from us. In contrast to this, the solution of particular a problem by the methods of statistical physics is based from the very beginning on atomic and molecular concepts and permits us to visualize the mechanism of the phenomenon involved.

The statistical approach allows one in principle to solve problems that cannot be solved at all within the framework of the thermodynamic method; the most important examples of this kind are the derivation of the equation of the state of macroscopic systems, the theory of heat capacity, some problems of the theory of thermal radiation. Finally, the statistical method permits, on the one hand, a rigorous substantiation of the laws of thermodynamics, and on the other hand, makes it possible to set the limits of applicability of the laws, and also to predict violations of the laws of classical thermodynamics (fluctuations) and estimate their scale.

It is clear from the above that neither thermodynamics nor statistical physics are restricted to any particular field of physical phenomena, in contrast to optics, mechanics, electrodynamics and other branches of physics, being rather methods of studying any macroscopic system in a state of equilibrium.

The methods of statistical thermodynamics can be used in studying any systems consisting of a sufficiently large number of particles: gases, liquids, solids, plasma, electrolytes, light radiation and even heavy nuclei containing hundreds of nucleons.

The branches of physics concerned with non-equilibrium states and processes, i.e. *non-equilibrium thermodynamics* and *physical kinetics*, have been elaborated to a considerably lesser degree than statistical thermodynamics, but are rapidly developing especially over the last few years. Physical kinetics, in particular, studies the processes of relaxation (transition from a non-equilibrium state to an equilibrium one) and steady-state transport processes. Part I of the present book deals with the fundamentals of thermodynamics, Part II is devoted to the statistical theory of equilibrium systems, and Part III is concerned with the fundamentals of physical kinetics and non-equilibrium thermodynamics.

Finally, in Sections 22 through 31 the thermodynamics of systems with a variable amount of substance and especially the problem of phase equilibriums and phase transitions are considered.

1. Equilibrium States and Equilibrium Processes

By a thermodynamic system will be meant any macroscopic body in an equilibrium or close to equilibrium state.

The states of any thermodynamic system can be defined by means of a number of parameters. Thus, for instance, the states of a gas or liquid (homogeneous systems) can be set by means of the following parameters: P (pressure), V (volume), T (temperature); the state of a film of a liquid—with the aid of α (surface tension coefficient), σ (film area) and T (temperature). The state of a rod can be specified with the aid of parameters l (length), σ (cross-sectional area), f (tensile force), E (Young's modulus).

It should be noted, however, that not all parameters of a system necessarily have a definite meaning in any particular state. Consider, for instance, a vessel divided into two halves by a partition with a valve, initially the left-hand half of the vessel contains a gas and the other half of the vessel is evacuated. If we open the valve, a stream of gas will be forced through it. It is clear that during the first moments of this process the volume of gas is indefinite, with the density of the gas contained in the right-hand half of the vessel changing from point to point according to some intricate law. It is thus impossible to indicate the boundaries of the volume of the gas.

Also states are possible in which any parameter of a system differs at different points, so that no single value of this parameter exists for the system as a whole. It is possible to visualize a system, for instance, the temperature of which changes from point to point, or a gas whose pressure varies from point to point. Experiments show, however, that when a thermodynamic system is in such a state, there exist fluxes (heat flux, mass flux, etc.) and this state does not remain invariable, unless it is maintained artificially with the aid of heat-proof (impervious) partitions, gas-tight walls, etc. With the passage of time a state is established in which the value of each parameter of the system is the same at all points and remains constant as long as desired, provided the external conditions do not change. Such states are called *equilibrium states.* If no equilibrium is established and there exist in the system gradients of macroscopic parameters (pressure, density, temperature, etc.) such a state is referred to as a *non-equilibrium state.*

The process during which a thermodynamic system passes from a non-equilibrium to an equilibrium state is referred to as a *relaxation process.* The time it takes each system parameter to become the same over the entire volume of the system is known as the *relaxation time*

of the given parameter. The total relaxation time of a system, clearly, is the longest of the individual relaxation times. The relaxation times for various processes cannot be calculated within the framework of thermodynamics, since relaxation phenomena are essentially the processes of molecular (atomic, electron, etc.) transfer of energy, mass, momentum and of similar physical quantities. The evaluation of relaxation time, therefore, is a problem of physical kinetics.

Let us consider a process operating in a thermodynamic system at a rate that is considerably less than the rate of relaxation; this means that at any stage of the process there will be enough time for the parameters to equalize over the entire system and such a process will represent a continuous succession of equilibrium states infinitely close to each other. Processes this slow are called *equilibrium* or *quasi-static*. It is clear that all real processes are non-equilibrium ones, approaching equilibrium only to a greater or lesser extent.

It should also be noted that in the case of an equilibrium process the gradients of all parameters are equal to zero at any moment of time. It follows from this that by virtue of symmetry the process may operate in a system both in a forward and reverse direction (that is, in the direction in which any system parameter increases and decreases). For this reason an equilibrium process can be reversed in time, and during the reverse process the system will pass through the same succession of states as during the forward process, but in a reversed sequence. In this connection equilibrium processes are also referred to as reversible processes.

In thermodynamics graphical representation of states and processes is widely practised. So, for instance, when dealing with homogeneous systems (gas or liquid) the states of the system are depicted by points and processes by lines on a P-V plane. It is clear that such graphical representation is possible only for equilibrium states and equilibrium (reversible) processes, since system parameters (for instance, pressure) have definite values only in equilibrium states. Up to Chapter IX of this book only equilibrium processes will be considered, unless otherwise specified.

In concluding this section we note that the parameters describing a state of a system are not independent quantities, but are interrelated by one or several equations that are known as the *equations of state*. For instance, for a gas pressure, temperature and volume are interrelated as follows: $f(P, V, T) = 0$, while for a rod the magnitude of the tensile force, temperature and the length of the rod are interrelated. The form of the equations of state cannot be determined by thermodynamic methods, and the knowledge permitting their derivation comes from experiments or from other branches of theoretical physics (usually from statistical physics). However,

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the derivation of equations of state in statistical physics is also a very intricate problem that can be solved for no more than a small number of the simplest systems.

2. Temperature. The Temperature Principle

The concept of temperature has already been used in Sec. 1, an intuitive understanding of the concept being assumed. We will now adopt a stricter approach to its understanding.

The concept of temperature is based on a rather subjective and diffuse term—the degree of hotness of a body. The term can, however, be given a more objective meaning through a whole number of easily measured physical parameters depending on the degree of hotness. Examples of such parameters are the height of the column of liquid mercury in a glass tube, the pressure of a gas in a constant-volume vessel, the resistance of a conductor, the emissive power of a red-hot body, etc. The data obtained by measuring any of these parameters can be used to create an empirical thermometer, with the measurement scale for this conditional or empirical temperature being chosen arbitrarily. When using, for instance, a mercury glass thermometer, the name conditional temperature can be given to the height of the column of mercury, measured in any unit, or any monotonically increasing function of that height. It should also be noted that the field of application of each empirical thermometer is restricted (if only from one side). Thus the lower limit of applicability of a mercury thermometer is the mercury solidification point, the lower limit of applicability of a gas thermometer is the gas condensation point, the upper limit of applicability of a resistance thermometer is the fusion point (or the boiling point) of metal, etc. Due to the fact that these fields of application partly overlap, we can select one of the empirical thermometers as a basis to the determination of conditional temperature on some arbitrary scale for quite a wide temperature range.

Let us now introduce the concept of the *thermostat*. By a thermostat (thermorelay) will be meant a body whose heat capacity is great compared with that of any reference bodies with which the thermostat will be brought into contact. This means that, on the one hand, when brought into contact with reference bodies the conditional temperature of the thermostat does not change and, on the other hand, after a short relaxation time any reference body brought into contact with the thermostat acquires its temperature.

Let us place into a thermostat a vessel containing a gas and change its volume with the help of a piston, simultaneously measuring the pressure. Plotting the results in the form of points on a P-V plane, we obtain a curve (isotherm), the form of which depends essentially on the kind of a gas and on the conditional temperature of the ther-

mostat. Changing the conditional temperature of the thermostat and repeating each time the procedure described above we obtain a system, or family, of isotherms corresponding to different conditional temperatures τ_n (Fig. 1).

Let us write down the equations of the isotherms 1, 2, ... in the form $\varphi_1(P, V) = 0$, $\varphi_2(P, V) = 0$, ..., labelling the isotherms in a way that the number n increases with the rising conditional temperature.

Let us now turn to an infinitely dense network of isotherms, assuming that when passing from one isotherm to the adjoining one the change in the conditional temperature of the thermostat and, consequently, of the gas is infinitely small. The number of the isotherm must then be replaced by a continuously varying parameter τ, which we can take as the conditional (empirical) temperature.

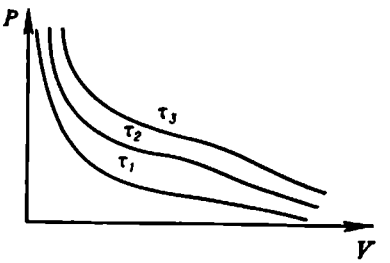


FIG. 1

Let the isotherm corresponding to the conditional temperature τ be described by the equation $\varphi(\tau \mid P, V) = 0$. Solving this implicit equation with respect to τ, we obtain $\tau = \tau(P, V)$. It has been shown experimentally that the isotherms of the same gas never intersect and, consequently, the conditional temperature is a single-valued function of state specified by parameters P and V.

It should be noted that conditional temperature may be introduced in a number of ways. Alongside the conditional temperature τ we can also use as the conditional temperature any monotonically increasing and continuous function $\tau' = f(\tau)$. This corresponds to a change (generally non-linear) in the temperature scale.

Experiments also show that at levels far from the gas liquefaction points (at high temperatures and low pressures) the isotherms can be approximately represented by equiangular hyperbolas

$$PV = \text{const} \tag{2.1}$$

and, consequently, $\tau = \tau(P, V)$. The equation $\tau = \tau(P, V)$ will be referred to as the *thermal equation of the state of substance* or, for the sake of brevity, as the *equation of state*. The imagined gas, for which the equation $\tau = \tau(P, V)$ is valid and the isotherms obey Eq. (2.1), is called a *thermally ideal* gas or briefly an *ideal gas*. It should be emphasized that real gases obey this equation only approximately, being closest to it when the temperature is high and the density of the gas low.

Thus, generalizing experimental data, we introduce the following postulate—the *temperature principle*: there exists (more than one) function of the state of a system that remains constant for any process operating in a thermostat, referred to as the conditional temperature.

3. Entropy. The Entropy Principle

A vessel with ideally heat-insulated walls and a piston will be referred to as an *adiabatic vessel*. Confining a gas in such a vessel, we can observe the development in it of an equilibrium process in conditions of heat insulation, that is of an *adiabatic process*.

Varying the volume of the gas by means of the piston and measuring the pressure, we use the data obtained to plot again on the P-V plane a curve called the *adiabat*. If we now disturb the heat insulation of the vessel, bringing it temporarily into contact with a body at a higher or lower conditional temperature, then restore the insulation and repeat the procedure described above, we can plot a second adiabat. Continuing the process we plot a whole set of adiabats on the P-V plane (Fig. 2) just as when establishing the processes at work in a thermostat we have obtained a set of isotherms.

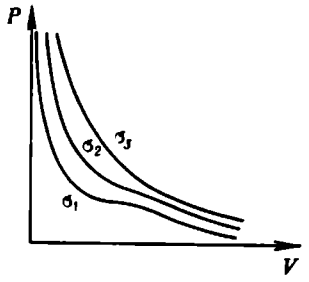


FIG. 2

Let us write down the equations of the adiabats numbered 1, 2, ... in the form $\psi_1(P, V) = 0$, $\psi_2(P, V) = 0$, labelling the adiabats in a way that to pass from the nth adiabat to the $(n + 1)$th adiabat we bring the adiabatic vessel into contact with a body at a higher temperature than its own.

Let us turn now to an infinitely dense set of adiabats, removing for this purpose the heat insulation of the adiabatic vessel for a short period of time and bringing the vessel into contact with a body that is at a slightly higher or lower temperature. Then, the number of the nth adiabat must be replaced by a continuously varying parameter σ, which will be referred to as the conditional entropy. Solving the equation $\psi(\sigma \mid P, V) = 0$ with respect to σ, we find $\sigma = \sigma(P, V)$. The quantity σ remains constant along each adiabat, and instead of the number n, the adiabats can be defined by setting the values of conditional entropy σ_1, σ_2, ...

It has been shown experimentally that the adiabats of the same gas never intersect and, consequently, conditional entropy is a single-valued function of state.

As with conditional temperature, conditional entropy can also be introduced in a number of ways. Any monotonically increasing and continuous function $\sigma' = f(\sigma)$ can be considered as the conditional entropy. Experimental findings also indicate another most important property of a network of isotherms and adiabats, namely, that each adiabat intersects each isotherm only at one point on the P-V plane.

It follows from this that the pairs of variables P, V and τ, σ are in a *one-to-one correspondence*. For each point on the P-V plane there exists one and only one pair of numbers τ, σ, since only one isotherm $\tau = \text{const}$ and one adiabat $\sigma = \text{const}$ pass through that point (the isotherms, just as adiabats, never intersect each other). On the contrary, if the state of the gas is represented on a τ-σ plane, then for each point on that plane there exists only one pair of numbers P, V, since the isotherm $\tau = \text{const}$ and the adiabat $\sigma = \text{const}$ cross each other and only at one point on the P-V plane. It follows from this that the state of the gas can be specified equally well by taking a pair of numbers τ, σ as a pair of numbers P, V and that the states of the gas can be depicted equally well on either the P-V plane or the τ-σ plane.

The adiabats of thermally ideal gases are described in any specified temperature range by the equation

$$PV^{\gamma} = \text{const}, \tag{3.1}$$

where the quantity $\gamma > 1$ is the *adiabatic exponent*, constant for a given gas. The law described by Eq. (3.1) is valid for monoatomic gases at any temperature lower than the characteristic temperature of gas ionization, and for polyatomic gases over a wide temperature range. In Sec. 8 it will be shown that γ is the ratio of the heat capacity at constant pressure, C_P, to the heat capacity at constant volume, C_V. The relation $\sigma = \sigma(P, V)$ will be referred to as the *caloric equation of the state of a substance*, and the imagined gas for which the equation $\sigma = \sigma(PV^{\gamma})$ is valid and for which the adiabats obey Eq. (3.1) as the *calorically ideal*, or *perfect, gas*. It should be noted that a perfect gas is necessarily a thermally ideal gas as well. Generally speaking, any statement to the contrary is incorrect, and the ratio C_P/C_V of a thermally ideal gas can depend on temperature over a wide temperature range.

By virtue of the fact that $\gamma > 1$, on the P-V plane the adiabats run steeper (3.1) in respect to the V-axis than the isotherms (2.1). For this reason the fundamental fact that each adiabat intersects each isotherm at one and only one point becomes insignificant for a perfect gas, since the system of equations $PV = a$, $PV^{\gamma} = b$ has one solution

$$V = \left(\frac{b}{a}\right)^{\frac{1}{\gamma-1}}, \quad P = \left(\frac{a^{\gamma}}{b}\right)^{\frac{1}{\gamma-1}}.$$

Generalizing experimental data, we are now in a position to formulate the following postulate of thermodynamics, the *entropy principle*: there exists (at least one) a single-valued function of state, remaining constant for any processes operating in a thermally-insulated vessel, called the conditional entropy. Between the pairs of variables, P, V and τ, σ there is a one-to-one correspondence. The conditional entropy of gases can be considered as a function of pressure and volume, $\sigma = \sigma(P, V)$. For a calorically ideal gas $\sigma = \sigma(PV^{\gamma})$; it depends only on the product PV^{γ}.

4. Absolute Temperature and Absolute Entropy

In the preceding sections conditional temperature and conditional entropy were defined accurate to the transformations $\tau' = f_1(\tau)$ and $\sigma' = f_2(\sigma)$, where f_1 and f_2 are monotonically increasing and continuous functions of their arguments.

Any arbitrariness in the selection of conditional temperature and conditional entropy can, however, be removed in the following way. The condition required for the one-to-one correspondence of pairs of variables P, V and τ, σ for two infinitely small regions on the P-V and τ-σ planes is known to be the difference of the Jacobian transformation $D = \partial(P, V)/\partial(\tau, \sigma)$ from zero and from infinity: $D \neq 0$, $D^{-1} \neq 0$ (see "Mathematical Appendix", A1).

The geometrical meaning of the Jacobian lies in the fact that its module gives the variation factor for the elementary area when passing from the P-V plane to the τ-σ plane

$$dP\,dV \rightarrow |D|\,d\tau\,d\sigma.$$

If we demand complete equivalence for the P-V and τ-σ planes, it is natural to impose the requirement that the Jacobian D be equal to unity. Such normalization of the Jacobian leads to a defined selection (accurate to the reference point and scale) of the temperature and entropy scales. The temperature and entropy read off these scales will be referred to as *absolute temperature* T and *absolute entropy* S (in the following sections the word "absolute" will be omitted for the sake of brevity).

It should be noted that there exist thermodynamic systems for which absolute temperature and absolute entropy cannot be calibrated over the entire P-V plane with the aid of the relationship

$$\frac{\partial(P, V)}{\partial(T, S)} = 1. \tag{4.1}$$

An example of such a system is water (see Sec. 18) and some other liquids and solids. This concerns, however, small regions of the P-V plane, while for the remaining parts of the plane calibration with the aid of Eq. (4.1) remains possible.

The requirement (4.1) allows the determination of temperature and entropy as a function of pressure and volume for any thermodynamic system for which the equations of the isotherms and adiabats are known. A perfect gas is used as a working medium for the calibration of absolute temperature and absolute entropy. Since the temperature of a perfect gas depends only on PV, and the entropy on PV^{γ}, then, denoting $PV = x$, and $PV^{\gamma} = y$, we obtain $T = T(x)$, $S = S(y)$ and

$$\frac{\partial(T, S)}{\partial(P, V)} = T'S'(\gamma - 1)y = 1, \quad T' = \frac{1}{S'(\gamma - 1)y}. \tag{4.2}$$

The symbols T' and S' in Eqs. (4.2) represent the derivatives of $T(x)$ and $S(y)$ with respect to their arguments. Since the right-hand side of Eq. (4.2) depends only on y and the left-hand side only on x, each of the two sides is equal to the same constant $\frac{1}{R}$. Then we get the equations

$$T'(x) = \frac{1}{R}, \quad S'(y) = \frac{R}{(\gamma - 1)y}, \tag{4.3}$$

following the integration of which we find

$$T = \frac{x}{R} + \theta = \frac{PV}{R} + \theta,$$

$$S = \frac{R}{\gamma - 1} \ln y + C = \frac{R}{\gamma - 1} \ln (PV^{\gamma}) + C, \tag{4.4}$$

where θ and C are integration constants. Since it is convenient to have a dimensionless number as an argument in the logarithm, we select the constant C equal to

$$S_0 = \frac{R}{\gamma - 1} \ln (P_0 V_0^{\gamma}).$$

Then Eqs. (4.4) are used to obtain

$$S - S_0 = \frac{R}{\gamma - 1} \ln \left(\frac{PV^{\gamma}}{P_0 V_0^{\gamma}} \right) = \frac{R}{\gamma - 1} \ln \frac{(T - \theta) V^{\gamma - 1}}{(T_0 - \theta) V_0^{\gamma - 1}}$$

$$= \frac{R}{\gamma - 1} \ln \left[\frac{(T - \theta)^{\gamma} P^{(1-\gamma)}}{(T_0 - \theta)^{\gamma} P_0^{(1-\gamma)}} \right], \tag{4.5}$$

where S_0, P_0, V_0, T_0 are the parameters of some arbitrary state. In this way we determine the absolute temperature and absolute entropy accurate to the reference point (the constants θ and S_0). The entropy constant remains arbitrary in thermodynamics and it can be measured only in statistical physics (see Sec. 40). In contrast to this the constant θ (as shall be proved in Sec. 8) is determined

unambiguously by the requirement that the heat capacity C_V should be constant and happens to be equal to zero $\theta = 0$.

In the following sections, up to Sec. 8 where we will prove this assertion, we will make use of this selection of the reference point for temperature. In particular, formulae (4.4), (4.5) take the form

$$PV = RT, \quad S - S_0 = \frac{R}{\gamma - 1} \ln \frac{PV^\gamma}{P_0 V_0^\gamma}$$

$$= \frac{R}{\gamma - 1} \ln \frac{TV^{\gamma-1}}{T_0 V_0^{\gamma-1}} = \frac{R}{\gamma - 1} \ln \frac{T^\gamma P^{1-\gamma}}{T_0^\gamma P_0^{1-\gamma}}. \tag{4.6}$$

The constant R determines only the range of the temperature and entropy scales, and when R is set at 8.31×10^3 J/deg·kmole, the temperature scale coincides with the Kelvin scale.

We determine in this way the absolute temperature and absolute entropy for ideal gases.

The concept of temperature can be applied to any thermodynamic system by the following trivial method. Take an ideal gas as a thermostat. Bringing any body in contact with it, by definition in its

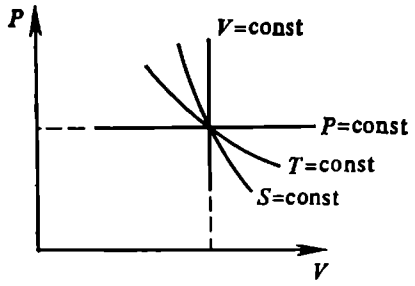


FIG. 3

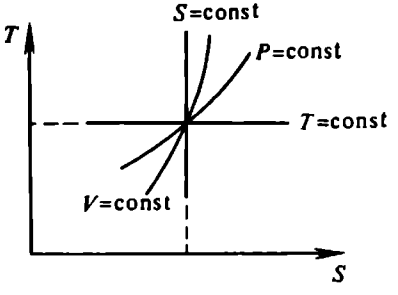


FIG. 4

capacity as a thermostat, we impart the temperature of the latter to the body involved. In essence, this means that we agree to measure the temperature of any system by means of a gas thermometer or, saying the same thing in a different way, with the aid of any empirical thermometer calibrated with a gas thermometer.

The problem of extending the concept of absolute entropy to any thermodynamic system will be considered in Sec. 10. Let us plot on P-V and T-S planes the isochores, isotherms and isoentropic curves (adiabats) for the particular case of a perfect gas.

The lines $V = \text{const}$, $P = \text{const}$, $T = \text{const}$, $S = \text{const}$ are represented on the P-V plane in Fig. 3 (the equation of the isotherm is $PV = \text{const}$ and of the adiabat $PV^\gamma = \text{const}$).

The equations for the isochore and isobar on the T-S plane are obtained by expressing P and V in terms of T and S by the equations

$$PV = RT, \quad PV^{\gamma} = \text{const}\, e^{(\gamma-1)S/R},$$

the second of the above equations following from Eq. (4.5) or Eq. (4.6).

Eliminating pressure or volume from these equations, we obtain a set of isochores and isobars on the T-S plane:

$$\text{at } V = \text{const}, \quad T = T_1(V)\, e^{(\gamma-1)S/R},$$

$$\text{at } P = \text{const}, \quad T = T_2(P)\, e^{(\gamma-1)S/\gamma R},$$

where $T_1(V)$ and $T_2(P)$ have the dimension of temperature.

On the T-S plane we have two sets of exponential curves (Fig. 4). Since $\gamma > 1$, the isochores are steeper with respect to the S-axis than the isobars.

Problems

1. The equation of the process undergone by a perfect gas is given on the P-V plane: $P = P_1 + \alpha V$ (P_1 and α are constants). Find the equation representing this process on the T-S plane.

Answer: $S = \dfrac{R}{\gamma - 1} \ln \dfrac{T}{T_0} + R \ln \dfrac{\sqrt{P_1^2 + 4\alpha RT} - P_1}{2\alpha V_0} + S_0.$

2. The equation of a straight line represented on the T-S plane is $T = \alpha S$. Find the corresponding process on the P-V plane.

Answer: $PV = \dfrac{\alpha R}{\gamma - 1} \ln \dfrac{PV^{\gamma}}{P_0 V_0^{\gamma}} + \alpha R S_0.$

b) Work

The concept of work has come to thermodynamics from mechanics. If a force f is applied in a situation of one-dimensional motion, then the elementary work is determined by the formula

$$\delta A = f\, dx.$$

It should be noted that even in mechanics the expression for elementary work is, strictly speaking, no more the differential of some function of the coordinate x, since the force may depend explicitly not only on x, but also on time and on the derivatives of x with respect to time; in this case non-potential forces are said to be involved.

When a gas undergoes expansion or compression, the work done is expressed by the well-known formula

$$\delta A = P\, dV. \tag{5.1}$$

Just as in mechanics, the expression (5.1) is generally not the differential of any function of the state of the gas. This becomes particularly clear upon examination of the graphical representation of work on a P-V diagram. The work involved in the expansion of a gas from volume V_1 to volume V_2 is

$$A = \int_{V_1}^{V_2} P\,dV \tag{5.2}$$

and is represented graphically by the area below the curve $P(V)$ shown in Fig. 5.

Since the pressure of a gas is not determined uniquely by its volume, and is a function of the state of the gas (which can be given, for instance, by the variables V and T), the pressure at intermediate points may be higher or lower than the pressure indicated on graph I (see graphs II and III) and, consequently, the work involved in the process is not determined by the initial and final states of the gas but depends on the entire course of the process. It follows that the line integral (5.2) depends on the path of integration and the integrand (5.1) is not a total differential of any function of the state of the gas. The physical meaning of this is that no quantity A (the work accumulated in the gas in its given state) exists whose increase or decrease would be equal to the quantity δA. This fact is emphasized by denoting the infinitely small amount of work by the symbol δA, and not by dA. In contrast to such quantities as T, S, P, V, that are functions of the state of the gas, work is a function of the process and it acquires a physical meaning when the conditions of gas compression or expansion are indicated.

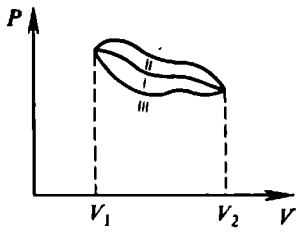


FIG. 5

So, for a perfect gas we have:

Isothermal process: $P_1V_1 = P_2V_2 = PV$,

$$A_T = \int_{V_1}^{V_2} P\,dV = P_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = P_1V_1 \ln \frac{V_2}{V_1} = RT \ln \frac{V_2}{V_1}. \tag{5.3}$$

Adiabatic process: $P_1V_1^\gamma = P_2V_2^\gamma = PV^\gamma$,

$$A_S = P_1V_1^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \frac{P_1V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] = \frac{RT_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]. \tag{5.4}$$

Isobaric process: $P_1 = P_2 = P$,

$$A_P = P \int_{V_1}^{V_2} dV = P(V_2 - V_1) = R(T_2 - T_1). \tag{5.5}$$

Isochoric process: $V_1 = V_2 = V$,

$$A_V = 0. \tag{5.6}$$

Problem

A perfect gas is contained in a cylinder closed by a piston with a cross-sectional area σ. The external pressure is constant and equal to P_0. An external force lifts the piston from height h_1 to height h_2 (a) isothermally; (b) adiabatically. Find the work done by the applied force on the gas.

Answer. (a) $A_T = P_0\sigma\left[h_2 - h_1 - h_1 \ln \frac{h_2}{h_1}\right]$;

(b) $A_S = P_0\sigma\left\{h_2 - \frac{\gamma h_1}{\gamma - 1}\left[1 - \frac{1}{\gamma}\left(\frac{h_1}{h_2}\right)^{\gamma-1}\right]\right\}$.

6. Adiabatic and Isothermal Potentials

Let us turn again to the mechanical analogy and assume that the force (in the case of one-dimensional motion) is a function only of the coordinate x. Then, the expression for elementary work, $\delta A = f\,dx$, can be represented as the decrease in some function $\mathcal{U}(x)$ referred to as the potential of force f or the potential energy

$$\delta A = f\,dx = -d\mathcal{U}(x),$$

whence

$$f = -\frac{\partial \mathcal{U}}{\partial x}.$$

In thermodynamics, as follows from formula (5.1), the role of force is played by pressure P and the role of the coordinate by volume V. By analogy with the mechanical potential, let us introduce the *thermodynamic potentials* in a way that the derivative of the thermodynamic potential with respect to volume is equal to pressure with an opposite sign.

The potential thus introduced depends on the additional conditions under which a gas undergoes compression or expansion. It is, however, necessary that each introduced potential be a single-valued function of the state of the gas. Let us consider two particular cases.

Adiabatic process. Let us equate the work done in an adiabatic process to the decrease in the *adiabatic potential*, denoting it by

U. We have

$$\delta A_S = P\,dV_S = -\,dU_S.^1 \tag{6.1}$$

In the case of an arbitrary non-adiabatic process an obvious generalization of formula (6.1) is the equation

$$dU = -P\,dV + \alpha\,dS. \tag{6.2}$$

Since the expression (6.2) must be a total differential, then

$$\left(\frac{\partial \alpha}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V;$$

it can be rewritten to read

$$\frac{\partial(\alpha, S)}{\partial(V, S)} = \frac{\partial(P, V)}{\partial(V, S)},$$

whence, making use of Jacobian properties, we find

$$\frac{\partial(\alpha, S)}{\partial(P, V)} = 1.$$

Multiplying both sides of the above equality by the Jacobian $\frac{\partial(P, V)}{\partial(T, S)}$ equal to unity, we obtain

$$\frac{\partial(\alpha, S)}{\partial(T, S)} = \left(\frac{\partial \alpha}{\partial T}\right)_S = 1, \quad \alpha = T + \varphi(S),$$

where $\varphi(S)$ is an arbitrary function of entropy. By virtue of formula (6.2) the adiabatic potential is also determined accurate to the arbitrary function of entropy $\int \varphi(S)\,dS$, which is not surprising, since the requirement $dU_S = -P\,dV_S$ remains satisfied. Thus, there exist an infinite number of adiabatic potentials differing from one another by the function of entropy. We normalize U, assuming $\varphi(S) \equiv 0$, $\alpha = T$. Then,

$$dU = T\,dS - P\,dV. \tag{6.3}$$

It follows from this that the natural or "own" variables of the adiabatic potential are entropy and volume and the derivatives with respect to these variables are equal to

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S. \tag{6.4}$$

Isothermal process. Equating the work done in an isothermal process, δA_T, to the decrease in the *isothermal potential* F, we get

$$\delta A_T = P\,dV_T = -\,dF_T.$$

For an arbitrary non-isothermal process a natural generalization of the above equation is the relationship

$$dF = \beta\,dT - P\,dV.$$

Since this expression must be a total differential, we have

$$\left(\frac{\partial \beta}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V,$$

or, passing to Jacobians,

$$\frac{\partial(\beta, T)}{\partial(V, T)} = \frac{\partial(P, V)}{\partial(V, T)}, \quad \frac{\partial(\beta, T)}{\partial(P, V)} = 1.$$

Multiplying both sides of the above equation by the Jacobian $\frac{\partial(P, V)}{\partial(T, S)} = 1$, we obtain

$$\frac{\partial(\beta, T)}{\partial(T, S)} = -\left(\frac{\partial \beta}{\partial S}\right)_T = 1, \quad \beta = -S + \psi(T).$$

Thus, there exists an infinite set of isothermal potentials, differing from one another by an arbitrary function of temperature (the requirement $dF_T = -P\,dV_T$ is satisfied for all these potentials). Normalize the choice of isothermal potential by the requirement $\psi(T) = 0$, $\beta = -S$. Then,

$$dF = -S\,dT - P\,dV. \tag{6.5}$$

It can be seen from Eq. (6.5) that the natural variables for the isothermal potential are temperature and volume, and the derivatives with respect to these variables are

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{6.6}$$

Let us relate the adiabatic and isothermal potentials. Subtracting from Eq. (6.3) the expression (6.5), we find that

$$d(U - F) = T\,dS + S\,dT = d(TS),$$

whence it follows that

$$F = U - TS, \tag{6.7}$$

where the integration constant is assumed to be equal to zero.

Problem

Making use of the expression for entropy (4.6), find the internal energy of a perfect gas (a) as a function of T; (b) as a function of its "own" variables S, V; and (c) the free energy in terms of its "own" variables T, V.

Answer. (a) $U - U_0 = \frac{R(T - T_0)}{\gamma - 1}$;

(b) $U - U_0 = \frac{RT_0}{\gamma - 1}\left[\left(\frac{V_0}{V}\right)^{\gamma - 1} e^{(\gamma - 1)(S - S_0)/R} - 1\right]$;

(c) $F - F_0 = \frac{R(T - T_0)}{\gamma - 1} - \frac{RT}{\gamma - 1} \ln \frac{TV^{\gamma - 1}}{T_0 V_0^{\gamma - 1}}$.

7. The Energy Principle. Supply and Removal of Heat

Let us introduce the concept of the *internal energy* of a thermodynamic system, defining it as the total energy less the kinetic and potential energies of the system as a whole. The internal energy of a system can be changed in two physically different ways: (1) by performing work δA on a gas by a gas or applied forces; (2) by bringing the gas into contact with a body at a higher temperature (heater) or with a body at a lower temperature (cooler). If no work is performed in this case, then the amount of energy obtained (or lost) by the gas is said to be the *quantity of heat* supplied to (or removed from) the gas due to such contact, denoted by the symbol δQ.

This assertion, being in essence the law of conservation of energy, will be referred to as the *energy principle* or the first law of thermodynamics.

It should be noted here that for processes operating in an ideally heat-insulated vessel the second method of converting energy is not valid and work is done at the expense of internal energy. This means that the adiabatic potential U introduced in Sec. 6 is identical to internal energy.

Thus, the energy principle may be formulated as follows:

$$dU = \delta Q - \delta A = \delta Q - P\ dV, \tag{7.1}$$

with the quantity of heat being regarded as positive when it is supplied to a system, and negative when it is removed from a system. Comparing formulae (7.1) and (6.3), we find the formula relating the quantity of heat δQ and the differential of entropy:

$$\delta Q = T\ dS. \tag{7.2}$$

It should be emphasized that formula (7.1) differs from formula (7.2), on the one hand, and from formula

$$dU = T\ dS - P\ dV, \tag{7.3}$$

on the other hand, in the following manner. Inasmuch as formula (7.1) is a special form of the law of conservation and conversion of energy, it is valid for any processes, both equilibrium (reversible) and non-equilibrium (irreversible). In contrast to this formulae (7.2) and (7.3) are valid only for equilibrium processes, and in the case of non-equilibrium processes, as will be shown in Sec. 23, they must be replaced with some inequalities. On the other hand, restricting ourselves to the investigation of equilibrium processes only, we must recognize that the content of equation (7.3) is much wider than that of formula (7.1), since equation (7.3) is based essentially

on the postulates of the existence of temperature and entropy, relating, thereby, the temperature, entropy and energy principles. In this connection relationship (7.3) is often referred to as the basic thermodynamic identity (for equilibrium processes).

It should be noted that the calibration requirement $\frac{\partial (T, S)}{\partial (P, V)} = 1$ [see Eq. (4.1)] is in a certain sense a corollary of Eq. (7.3). It represents the condition required for the right-hand side of Eq. (7.3) to be a total differential, although only when the derivative $\left(\frac{\partial P}{\partial S}\right)_V$ differs from zero. As will be shown in Sec. 18, this inequality may be violated for a number of substances at some points on the P V plane.

Formula (7.2) is similar to the formula for elementary work $\delta A = P\,dV$ [see (5.1)]. In view of this similarity Gibbs has suggested that entropy S be considered as a thermodynamic coordinate and temperature T be called a thermodynamic force. Just as work is related to a change in a mechanical coordinate, so the supply or removal of heat is related to a change in the thermodynamic coordinate, entropy.

The heat supply to a system is equivalent to an increase in the thermodynamic coordinate, the increase of entropy, and the removal of heat from a system is equivalent to a decrease in the thermodynamic coordinate, removal of entropy. The thermodynamics of equilibrium processes can be said to be in a way an extension of mechanics, associated with the introduction of an additional non-mechanical degree of freedom. While the mechanics of one-dimensional motion admits only the variation of the coordinate x (variation of volume V in gas mechanics), thermodynamics also deals with a change in entropy S, signifying the supply or removal of heat.

The isothermal potential F is also called the *free energy*, and the difference $U - F = TS$ the *bound energy*. These names arise from the fact that F can be specified as the fraction of internal energy spent to produce work in an isothermal process, while the decrease in the fraction TS, equal to $-T\,dS$ at $T = \text{const}$, is compensated for by the supplied heat $T\,dS$.

Let us analyze in greater detail formula (7.2). The geometric interpretation of the quantity of heat represented on a T-S diagram is in perfect analogy with the interpretation of work on a P-V diagram. It is exactly the quantity of heat supplied to a system that is expressed analytically by formula

$$Q = \int_{S_1}^{S_2} T\,dS, \tag{7.4}$$

and represented graphically by the area below the curve $T(S)$ (Fig. 6).

Since temperature is a function not only of entropy, but also of the state of a gas (for instance, a function of S and V, or a function of S and P), the area (quantity of heat) depends not only on the initial and final states, but also on the entire course of the process. In the intermediate states of a process the temperature may be both higher and lower than the temperature corresponding to curve I. This is why the quantity of heat involved in the processes represented by curves II, III, etc. will respectively be greater or smaller than the quantity of heat corresponding to curve I. This means that the line integral (7.4) depends not only on the initial and final points, but also on the entire path of integration. It follows that the integrand $\delta Q = T\,dS$ is not a total differential of any function of the state of the gas. The physical meaning of the above assertion is that just as the concept of work "accumulated" in a gas in some of its states has no meaning, no quantity of heat Q exists whose increase or decrease would be equal to the quantity δQ. (Just as in the case of work, this is emphasized by denoting an infinitely small amount of heat by δQ and not dQ.)

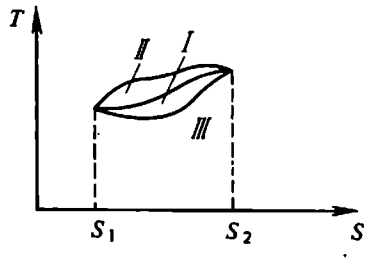


FIG. 6

Similar to work, *the quantity of heat is a function of a process* and it acquires an unambiguous meaning only when the conditions of heating or cooling of a gas are specified. In this way both the work and the quantity of heat are functions of a process and not of the state of the gas involved, and the quantities $P\,dV$ and $T\,dS$ are generally not total differentials. Only the difference $T\,dS - P\,dV$ is a total differential of the adiabatic potential, internal energy, that is, a function of the state of a gas. Consequently, the concepts of the supply of work and of the supply of heat in a gas are meaningless, only the energy supply having a meaning.

Using a method similar to that applied to work, we will now show how to calculate the quantity of heat supplied or removed in different thermodynamic processes.

Isothermal process.

$$Q_T = \int_{S_1}^{S_2} T\,dS = T(S_2 - S_1). \tag{7.5}$$

Using formula (4.6) for entropy and the Boyle law

$$S - S_0 = \frac{R}{\gamma - 1} \ln \left(\frac{PV^\gamma}{P_0 V_0^\gamma} \right), \quad P_1 V_1 = P_2 V_2,$$

we obtain

$$Q_T = \frac{RT}{\gamma - 1} \ln \left(\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma} \right) = RT \ln \left(\frac{V_2}{V_1} \right). \tag{7.6}$$

Isobaric process. From formula (4.6) we find that at $P = \text{const}$ $dS = \frac{R\gamma\, dV}{(\gamma - 1) V}$ and

$$Q_P = \frac{R\gamma}{\gamma - 1} \int_{V_1}^{V_2} \frac{T\, dV}{V} = \frac{P\gamma}{\gamma - 1} \int_{V_1}^{V_2} dV = \frac{\gamma P}{\gamma - 1} (V_2 - V_1) = \frac{\gamma R}{\gamma - 1} (T_2 - T_1). \tag{7.7}$$

Isochoric process. From formula (4.6) we find that at $V = \text{const}$ $dS = \frac{R\, dP}{(\gamma - 1) P}$ and

$$Q_V = \frac{R}{\gamma - 1} \int_{P_1}^{P_2} \frac{T\, dP}{P} = \frac{V}{\gamma - 1} (P_2 - P_1) = \frac{R (T_2 - T_1)}{\gamma - 1}. \tag{7.8}$$

Adiabatic process.

$$Q_S = 0.$$

8. Heat Capacity of Gases

Let us introduce the concept of the *heat capacity* of a gas, defining it as the quantity of heat that must be supplied to the gas to raise its temperature by one degree (1°):

$$C = \frac{\delta Q}{\delta T}. \tag{8.1}$$

It is clear that, like the quantity of heat, *heat capacity is a function of a process*, acquiring an unambiguous meaning when the conditions of the heating of the gas are specified.

Examples of heat capacity are the heat capacity at constant pressure C_P and at constant volume C_V. By virtue of the condition $\delta Q = 0$ the adiabatic process is associated with the heat capacity equal to zero, $C_S = 0$. Finally, the isothermal process ($T = \text{const}$) can be conditionally assigned the heat capacity $C_T = \pm\infty$, taking this process as the limiting case of a process in which temperature rises or drops at an exceedingly low rate upon heat supply ($\delta Q > 0$, $\delta T = \pm \varepsilon$, $|\varepsilon| \to 0$). Since gas heating conditions can be infinitely varied (so that not P, V, S will remain constant, but the

arbitrary functions of P and V), there exists an infinite set of heat capacities of a gas. It should be noted, in particular, that processes for which heat capacity is negative (δQ and δT have opposite sings) are possible. This is so when a heated gas expands sufficiently and produces an amount of work exceeding the quantity of heat supplied to the gas. Then, notwithstanding the supply of heat, the internal energy and temperature of the gas will decrease, and the ratio $\frac{\delta Q}{\delta T}$ will be negative. Let us find the heat capacities C_V and C_P, expressing them in terms of the derivatives with respect to entropy. According to (7.2), we have

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P. \tag{8.2}$$

Let us calculate the heat capacities C_V and C_P of a perfect gas and prove that the constant θ in the expression for the absolute temperature, $T = \frac{PV}{R} + \theta$, must be chosen equal to zero. Differentiating with respect to T the entropy formula (4.5)

$$S - S_0 = \frac{R}{\gamma - 1} \ln\left[\frac{(T-\theta)\,V^{\gamma-1}}{(T_0-\theta)\,V_0^{\gamma-1}}\right] = \frac{R}{\gamma-1}\ln\left[\frac{(T-\theta)^{\gamma} P^{1-\gamma}}{(T_0-\theta)^{\gamma} P_0^{1-\gamma}}\right]$$

first at $V = \text{const}$ and then at $P = \text{const}$ and, making use of formulae (8.2), we find

$$C_V = \frac{R}{\gamma-1}\frac{T}{T-\theta}, \quad C_P = \frac{R\gamma T}{(\gamma-1)(T-\theta)}. \tag{8.3}$$

It can be seen from Eqs. (8.3) that the heat capacities C_V and C_P are constant only at $\theta = 0$; in this case

$$C_V = \frac{R}{\gamma-1}, \quad C_P = \frac{R\gamma}{\gamma-1}, \tag{8.4}$$

whence

$$\frac{C_P}{C_V} = \gamma \tag{8.5}$$

and

$$C_P - C_V = R. \tag{8.6}$$

Formula (8.6) is known as *Mayer's equation**.

* In the nineteenth century Eq. (8.6) was used to determine the mechanical equivalent of heat J and its reciprocal quantity A —the heat equivalent of work. For this purpose it is sufficient to measure for some gas the difference $C_P - C_V$ (in calories) at a distance far from the liquefaction point, and the gas constant R in mechanical units (joules). Such experiments conducted with different gases over a wide range of temperatures and pressures invariably yielded the same result, $J = 0.239$ J/cal, this being the first substantiation of the energy principle.

Thus, we have determined the reference point for the absolute temperature; we draw the attention of the reader to the fact that for this purpose, in addition to measuring pressure and volume (the construction of the network of isotherms in a thermostat and the network of adiabats in an adiabatic vessel), we had to measure one caloric quantity, the heat capacity C_V (or C_P) and make sure that it was independent of temperature. The situation would not change if we were to choose as a working medium for the calibration of the temperature and entropy scales not a perfect gas, but another thermodynamic system. In this case, to determine the temperature reference point we would also have to base our study on one calorimetric measurement in addition to measuring pressures and volumes. The basic reason for such a procedure consists in that the thermodynamic determination of the temperature scale is based in the final analysis on formula (7.2). It can easily be seen that this formula is not invariant in respect to the shift of the temperature reference point and presupposes a definite choice of the quantity θ, namely $\theta = 0$.

9. Cyclic Processes. The Carnot Cycle

Let us consider on a P-V plane a reversible (equilibrium) cyclic process, or cycle (Fig. 7), and let the point representing the state of the gas undergoing the process pass through the cycle in the clockwise direction. Along the path abc the gas expands and, according to Eq. (5.2), performs positive work measured by the area below the curve abc. Along the path cda the gas is compressed by external forces that perform negative work, the absolute value of which is measured by the area below the curve cda. With the direction of the cycle selected and upon its completion, there is a gain in work A measured by the area contained within the cycle $abcda$. Consider the same cyclic process represented on a T-S plane (Fig. 8). The cycle is, evidently, represented by another closed curve $a'b'c'd'a'$. Suppose that the representative point passes through the cycle in the same way as on the P-V plane, i.e. in a clockwise direction (it will be shown later that a contrary assumption would lead us into contradiction). Then, entropy increases along the path $a'b'c'$ and, according to formula (7.4), heat is supplied to the gas, with the quantity of supplied heat being measured by the area below the curve $a'b'c'$. Entropy diminishes along the section $c'd'a'$ and heat is removed from the gas. The absolute value of the removed heat is represented on the diagram by the area below the curve $c'd'a'$. Upon completion of the entire cycle there is an excess quantity of heat that is measured by the area contained within the closed curve $a'b'c'd'a'$.

According to the energy principle (7.1), we have

$$\oint \delta Q = \oint dU + \oint \delta A.$$

Since the internal energy is a function of the state of the gas, $\oint dU = 0$ and consequently

$$Q = A. \tag{9.1}$$

Thus, the areas of the cycles plotted on the P-V and T-S planes, or diagrams, must be equal to each other (it will be noted that we also

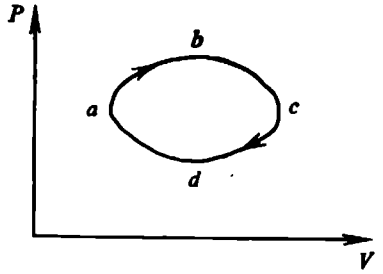


FIG. 7

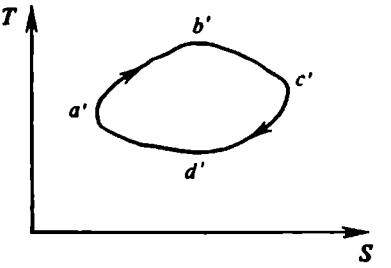


FIG. 8

prove, thereby, that the direction of the cycle depicted on the P-V and T-S planes must be the same, otherwise we would obtain a physically and mathematically meaningless equality of positive work and negative heat).

Thus, a cyclic process in which a representing point runs clockwise through the cycle represents schematically the performance

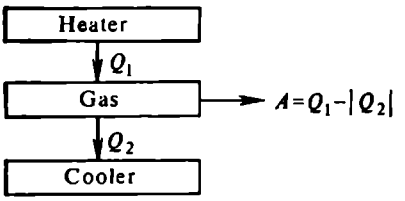


FIG. 9

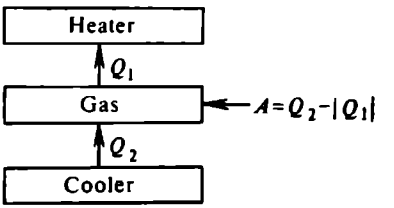


FIG. 10

of any heat engine converting heat into work (Fig. 9). The gas receives from the heater the quantity of heat Q_1, a fraction of this heat Q_2 ($Q_2 < 0$) is removed by the cooler, and the difference $Q_1 - |Q_2|$ is converted into work. It follows from formula (9.1) that if $Q = 0$, then $A = 0$ as well. Thus, it is impossible to construct a heat engine that would provide a gain in work with no energy supply from

its environment (a perpetual motion machine of the first kind). It is clear that it is reasonable to define the efficiency of a heat engine as the ratio of the work A to the quantity of heat Q_1 received from the heater:

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1}. \tag{9.2}$$

If we now consider a cycle proceeding in an anticlockwise direction, all processes develop in opposite directions and the quantities of heat and work have opposite signs. We obtain the performance diagram of a cooler that consumes work, but transfers heat from a body at a lower temperature to a body at a higher temperature ($Q_1 > 0$) (Fig. 10).

Let us consider by way of example the so-called *Carnot cycle* consisting of two adiabats and two isotherms. Figures 11 and 12 show the Carnot cycle plotted on P-V and T-S planes. It can be

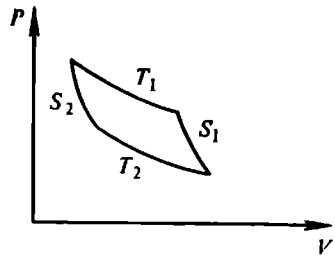


FIG. 11

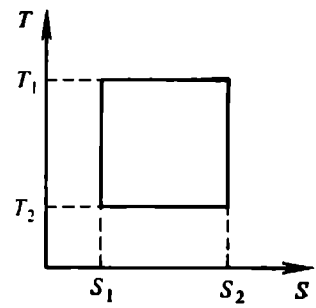


FIG. 12

seen that while on the P-V plane the form, or outline, of the cycle depends on the kind of the gas involved, and particularly on whether the gas is real or ideal, the Carnot cycle for any thermodynamic system is represented on the T-S plane by a rectangle whose sides are parallel to corresponding coordinate axes.

Let us calculate the efficiency of a reversible Carnot cycle. According to formula (7.5), we have

$$Q_1 = T_1(S_2 - S_1),\ Q_2 = T_2(S_1 - S_2),$$

whence

$$\eta = \frac{Q_1 - |Q_2|}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (Q_1 > 0,\ Q_2 < 0). \tag{9.3}$$

The following corollaries result from formula (9.3).

1 The efficiency of a Carnot cycle is independent of the working medium involved.

2. The efficiency of a Carnot cycle depends on the ratio of the temperatures of the heater and the cooler and is independent of the component parts of the heat engine. The lower the ratio $\frac{T_2}{T_1}$ the higher the efficiency of the Carnot cycle.

3. The efficiency of a Carnot cycle is always less than unity, and it approaches unity as the temperature of the cooler tends to absolute zero.

It will be noted that the Carnot cycle is the natural and only possible working cycle for a heat engine incorporating one constant-temperature heater and one constant-temperature cooler, since for such a machine heat must be absorbed and removed isothermally and the intermediate processes must be achieved adiabatically. No other types of heaters or coolers exist.

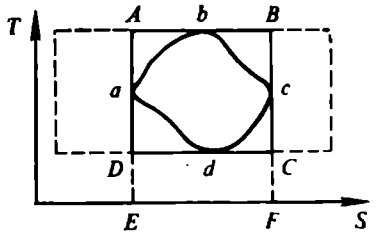


FIG. 13

Let us prove the following theorem: the efficiency of the Carnot cycle is higher than that of any other equilibrium cycle in which the maximum temperature of the heater and minimum temperature of the cooler are equal respectively to the temperature of the heater and temperature of the cooler involved in the Carnot cycle.

To prove this theorem let us depict the given cycle on a T-S plane (Fig. 13), plotting around it a Carnot cycle. Denote the sum of the areas aAb and bBc by q_1, and the sum of the areas aDd and cCd by $|q_2|$ ($q_2 < 0$). By definition, the efficiency of the Carnot cycle is

$$\eta_C = \frac{Q_1 - |Q_2|}{Q_1}, \tag{9.4}$$

where Q_1 is represented by the area of the rectangle $ABFE$, and $|Q_2|$ by the area of the rectangle $DCFE$. For the $abcda$ cycle we have

$$\eta = \frac{Q_1 - q_1 - |Q_2 + q_2|}{Q_1 - q_1}. \tag{9.5}$$

Substituting, in accordance with formula (9.4), $Q_1 - |Q_2| = \eta_C Q_1$ into the numerator of formula (9.5), we obtain

$$\eta = \frac{\eta_C Q_1 - q_1 - |q_2|}{Q_1 - q_1},$$

whence

$$\eta = \eta_C - \frac{q_1}{Q_1 - q_1}(1 - \eta_C) - \frac{|q_2|}{Q_1 - q_1}.$$

Since the second and third terms in the right-hand side of the above equation are negative ($\eta_C \leqslant 1$), then $\eta_C \geqslant \eta$, with the equality occurring only when $q_1 = q_2 = 0$, i.e. when the cycle fully coincides with the Carnot cycle.

It should be noted that not only the Carnot cycle described around the given cycle satisfies the conditions of the theorem, but also a Carnot cycle with adiabats located in a different way (see the dotted lines in Fig. 13). Since η_C does not depend on S_1 and S_2, the theorem remains valid for such cycles as well. We determined above that $\eta_C < 1$, therefore $\eta < 1$ for other cycles as well. From this follows one of the classic statements of the *second law of thermodynamics*: it is impossible to construct a perpetual motion machine of the second kind, i.e. a periodically acting machine that would convert all the heat supplied by a heater into work (that would have an efficiency equal to unity).

Such an imaginary machine would be able to perform at the expense of cooling the ocean or the earth crust and although its performance would not violate the law of conservation of energy (the machine would not be a perpetual motion machine of the first kind) it would practically be an unlimited source of energy. Laws of nature, however, make it impossible to construct such a machine. The conversion of heat into work requires that alongside with a heater there should exist a cooler, i.e. that there should exist a temperature difference.

Problem

For the cycles *I* (Fig. 14) and *II* (Fig. 15) realized with a perfect gas find (1) the quantity of heat and work involved in all

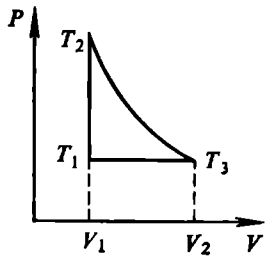


FIG. 14

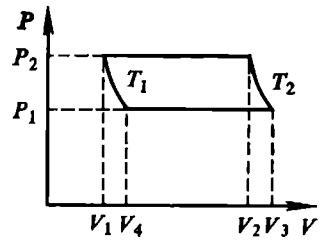


FIG. 15

sections of the cycle; (2) make sure that $Q = A$; (3) find the efficiency.

Answer: Cycle *I*: (2) $Q = A = C_V(T_2 - T_1) - C_P T_1 \left[\left(\frac{T_2}{T_1}\right)^{1/\gamma} - 1\right]$;

$$(3)\ \eta = 1 - \gamma \frac{(T_2/T_1)^{1/\gamma} - 1}{(T_2/T_1) - 1}.$$

Cycle *II*: (2) $Q = A = R(T_2 - T_1) \ln\left(\frac{V_3}{V_2}\right)$;

$$(3)\ \eta = \frac{R(T_2 - T_1)\ln(V_3/V_2)}{C_P(T_2 - T_1) + RT_2 \ln(V_3/V_2)}.$$

10. Axiomatics of Thermodynamics. Generalization of the Concept of Entropy to Arbitrary Thermodynamic Systems. Nernst's Heat Theorem

This section is devoted to some problems associated with a set of axioms of thermodynamics.

Since in this book use is made of a set of axioms differing from the traditional one, we find it useful to discuss here the set of principles or laws that is usually used in exposing classical thermodynamics, and find out how the system used by us is logically related to this set of axioms.

In traditional presentations the following postulates are used as a foundation for the whole building of classical thermodynamics:

1. *The zeroth law of thermodynamics* postulating the existence of temperature. It should be noted that the zeroth law is by far not always introduced in thermodynamics courses, although its logical necessity is obvious (see, for instance [1]-[3]).

2. *The first law of thermodynamics* expressing the principle of conservation of energy as applied to thermal processes

$$dU = \delta Q - \delta A. \tag{10.1}$$

3. *The second law of thermodynamics* admitting a considerable number of different, but equivalent statements. In the first place let us mention the earliest quantitative statements of this law suggested by Carnot, Clausius, Kelvin, Ostwald:

(a) heat can never pass from a colder to a warmer body without some other changes, connected therewith, occurring at the same time;

(b) it is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects;

(c) it is impossible to construct a perpetual motion machine of the second kind.

When applied to equilibrium processes any of these equivalent statements of the second law of thermodynamics leads to the existence of a function of the state of a system (entropy) that is related to the quantity of heat by [see Eq. (7.2)].

$$\delta Q = T\, dS. \tag{10.2}$$

Combining formulae (10.1) and (10.2), we obtain a compatible mathematical statement of the first and second laws of thermodynamics in the following form [see Eq. (7.3)]:

$$dU = T\,dS - P\,dV. \tag{10.3}$$

The condition for the right-hand side to be a total differential is the relationship

$$\frac{\partial(T, S)}{\partial(V, S)} = \frac{\partial(P, V)}{\partial(V; S)},$$

whence, at $\frac{\partial(P, V)}{\partial(V, S)} \neq 0$, we obtain the already known [Eq. (4.1)] calibration

$$\frac{\partial(T, S)}{\partial(P, V)} = 1. \tag{10.4}$$

Let us revert now to our set of axioms. We have postulated in the first place the existence of temperature and entropy (stated the temperature principle and the entropy principle). The calibration condition for absolute temperature and absolute entropy leads to the fact that the right-hand side of expression (7.3) is a total differential. Since for a process occurring in an adiabatic vessel this expression is $-P\,dV = \delta A$, the adiabatic potential U must be identified with the internal energy. Adding the energy principle (7.1) to our set of axioms, we obtain formula (7.2) as a corollary. Thus, in addition to the temperature principle and the entropy principle, and the calibration condition (10.4) relating them, the energy principle (the first law of thermodynamics) must be included into the set of axioms.

In spite of the fact that such a construction system for thermodynamics is not the most economical from the viewpoint of the number of axioms, we consider it to have certain methodical advantages consisting in that from the very beginning the existence of an internal relation between the concepts of temperature and entropy (T—thermodynamic force, S—thermodynamic coordinate), and the existence of symmetry between the two pairs of variables T, S and P, V is emphasized.

Let us mention one more possible method of introduction of absolute temperature and absolute entropy, not requiring the use of a perfect gas as a reference gas, to measure T and S. This method is based on the *Carathéodory principle*, according to which in the neighbourhood of equilibrium state A of a system there exist other states B which cannot be attained from state A by an adiabatic path—the *principle of adiabatic inaccesibility*. It should be noted that this principle is contained in our entropy principle. In fact, the assumption that the adiabats do not intersect each other means that two states represented on *different* adiabats cannot be linked by a third adiabatic process.

Consider two equilibrium thermodynamic systems 1 and 2 that are in contact with each other and have the same conditional temperatures $\tau_1 = \tau_2 = \tau$. (Otherwise, if $\tau_1 \neq \tau_2$, the systems should have been separated from each other by a movable heat-insulated partition. The Carathéodory principle may be violated for such thermally heterogeneous system.) The state of each system 1 and 2 is described by some thermodynamic parameters. Making use of the thermal and caloric equations of states we may assume that the first two parameters are τ and σ_i ($i = 1, 2$). Then the state of system 1 is given by the parameters τ, σ_1, x_1, the state of system 2, by the parameters τ, σ_2, x_2, and the state of the combined system, by the parameters τ, σ, x_1, x_2 (σ_1, σ_2, σ denote conditional entropies, x_1 and x_2 —totalities of the remaining thermodynamic parameters of systems 1 and 2 respectively).

Assume that in the course of some equilibrium process quantity of heat δQ is supplied to the combined system and quantities of heat δQ_1 and δQ_2 to the subsystems, so that

$$\delta Q = \delta Q_1 + \delta Q_2. \tag{10.5}$$

Since on any adiabat $\delta Q = 0$ and $d\sigma = 0$, then at small rates of heat transfer the quantities δQ, δQ_1, δQ_2 are proportional to $d\sigma$, $d\sigma_1$, $d\sigma_2$ respectively, and the coefficients may depend on the parameters of state and be positive:

$$\delta Q_1 = f_1(\tau, \sigma_1, x_1)\, d\sigma_1,\ \delta Q_2 = f_2(\tau, \sigma_2, x_2)\, d\sigma_2,\ \delta Q = f(\tau, \sigma, x_1, x_2)\, d\sigma. \tag{10.6}$$

Substituting the expressions (10.6) into (10.5), we get

$$d\sigma = \frac{f_1(\tau, \sigma_1, x_1)}{f(\tau, \sigma, x_1, x_2)} d\sigma_1 + \frac{f_2(\tau, \sigma_2, x_2)}{f(\tau, \sigma, x_1, x_2)} d\sigma_2. \tag{10.7}$$

Since the parameters x_i are independent of τ and σ_i, it follows from this that

(1) σ is a function only of σ_1 and σ_2, $\sigma = \sigma(\sigma_1, \sigma_2)$;

(2) the coefficients f_1, f_2, f depend only on the conditional temperature and conditional entropy $f_1 = f_1(\tau, \sigma_1)$, $f_2 = f_2(\tau, \sigma_2)$, $f = f(\tau, \sigma)$ and are independent of x_1, x_2.

(3) the ratios $f_1(\tau, \sigma_1)/f(\tau, \sigma)$ and $f_2(\tau, \sigma_2)/f(\tau, \sigma)$ are independent of τ.

It follows from the above property that

$$\frac{\partial}{\partial \tau}\left(\frac{f_i}{f}\right) = \frac{\frac{\partial f_i}{\partial \tau} f - f_i \frac{\partial f}{\partial \tau}}{f^2} = 0 \quad (i = 1, 2),$$

whence we find $\frac{\partial}{\partial \tau}(\ln f_i) = \frac{\partial}{\partial \tau}(\ln f) = \Omega(\tau)$ (since $\ln f_1$ is independent of σ_2, and $\ln f_2$ is independent of σ_1). Consequently, we have

$$f_1(\tau, \sigma_1) = \psi(\tau) F_1(\sigma_1),\ f_2(\tau, \sigma_2) = \psi(\tau) F_2(\sigma_2),\ f(\tau, \sigma) = \psi(\tau) F(\sigma), \tag{10.8}$$

where $\psi(\tau) = \exp\left[\int \Omega(\tau)\, d\tau\right]$ is an arbitrary positive function of τ. Substituting Eqs. (10.8) into Eq. (10.7), we find

$$F(\sigma)\, d\sigma = F_1(\sigma_1)\, d\sigma_1 + F_2(\sigma_2)\, d\sigma_2. \tag{10.9}$$

Determine now the absolute entropy S accurate to the reference point by the formula $S = \int F(\sigma)\, d\sigma$, and the absolute temperature, using the formula $T = \psi(\tau)$. Then from formulae (10.6) and (10.8) we find $\delta Q/T = dS$, i.e. the conventional statement of the second law of thermodynamics, and formula (10.9) is an indication of the additivity of the absolute entropy $dS = dS_1 + dS_2$, $S = S_1 + S_2$.

Let us find out now what degree of arbitrariness is allowed by formula (10.2) in the choice of absolute temperature and absolute entropy. Assume that two absolute temperatures, $T_1(\tau)$ and $T_2(\tau)$, and two absolute entropies, $S_1(\sigma)$ and $S_2(\sigma)$ are possible. Then, on the basis of formula (10.2),

$$\delta Q = T_1\, dS_1, = T_2\, dS_2,$$

or

$$\frac{T_2(\tau)}{T_1(\tau)} = \frac{dS_1(\sigma)}{dS_2(\sigma)}. \tag{10.10}$$

Since the left-hand side of Eq. (10.10) depends only on τ, and the right-hand side, only on σ, the two sides are equal to the same constant a and

$$T_2(\tau) = aT_1(\tau),\ dS_2(\sigma) = \frac{1}{a}\, dS_1(\sigma),\ S_2(\sigma) = \frac{1}{a}\, S_1(\sigma) + b.$$

Thus, the arbitrariness in determining absolute temperature and entropy consists only in that we can change simultaneously the "scale division" of the temperature and entropy scales a and a^{-1} times and choose arbitrarily the entropy reference point.

The concept of entropy can be generalized in principle to arbitrary thermodynamic systems with the aid of formula (10.2). In fact, assuming the value of entropy of the system under consideration in some arbitrarily chosen state to be equal to zero (arbitrary reference point for the entropy scale) and supplying to this system a quantity of heat δQ (in a reversible way, i.e., at an infinitely small temperature difference between the system and the heater), we can use formula $dS = \frac{\delta Q}{T}$ to graduate the entropy scale of any system.

Let us introduce one more important thermodynamic principle, known as the *Nernst heat theorem*, or the *third law of thermodynamics*. This principle cannot be proved within the framework of thermodynamics and is introduced in the way of a postulate as a generalization of some experimental data relating to chemical thermodynamics.

The Nernst's theorem can be proved within the framework of statistical physics and the proof is associated essentially with quantum-mechanical ideas. It will be considered in Secs. 39 and 63. Here we shall limit ourselves to the statement of the Nernst theorem and its thermodynamic corollaries.

The *Nernst heat theorem*: at absolute zero the entropy of any equilibrium system is constant, independent of any varying parameters (pressure, volume, field intensities, etc.).

In many cases this constant happens to be equal to zero and that is why the Nernst principle is often formulated as follows

$$S|_{T=0} = 0,$$

although this statement is not universal.

The Nernst heat theorem implies a number of important corollaries.

1. At $T = 0$ any heat capacity of a system approaches zero. In fact, at a temperature close to absolute zero, the entropy can be presented in the form

$$S(T) = S(0) + A(x)\, T^n,$$

where $S(0)$ = a constant independent of any variable parameters;
x = a parameter assumed to be constant when calculating the heat capacity (V, P, etc.).

According to the formula $C_x = T\left(\frac{\partial S}{\partial T}\right)_x$, we have

$$C_x(T) = nA(x)\, T^n$$

and, consequently,

$$C_x(0) = 0.$$

2. The thermal expansion coefficient $\left(\frac{\partial V}{\partial T}\right)_P$ approaches zero at $T = 0$. In fact, taking into account the basic thermodynamic identity (10.4), we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial(V, P)}{\partial(T, P)} = \frac{\partial(S, T)}{\partial(T, P)} = -\left(\frac{\partial S}{\partial P}\right)_T \xrightarrow[T\to 0]{} 0,$$

since at $T = 0$ the entropy is independent of pressure.

3. The pressure coefficient $\left(\frac{\partial P}{\partial T}\right)_V$ approaches zero at $T = 0$:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P, V)}{\partial(T, V)} = \frac{\partial(T, S)}{\partial(T, V)} = \left(\frac{\partial S}{\partial V}\right)_T \xrightarrow[T\to 0]{} 0.$$

4. Unattainability of absolute zero.

The Nernst heat theorem is often referred to as the *absolute zero unattainability principle* for the following reason. Let us take a Carnot cycle in which the cooler is at a temperature $T_2 = 0$. For this

reversible machine the total change in entropy in the cycle would be equal to its change in the region of isothermal heating $T = T_1$:

$$\Delta S = \int \frac{\delta Q}{T_1} = \frac{Q_1}{T_1},$$

since the region of isothermal cooling $T = T_2 = 0$ is an isentropic curve $S = 0$ and the other two processes of the cycle are isentropic. But, on the other hand, the total change in entropy in the cycle

$$\Delta S = \oint dS = 0.$$

The arising contradiction ($Q_1 \neq 0$) proves the unattainability of the zero isotherm $T = 0$ which is simultaneously an isentropic curve (adiabat) at $S = 0$ or $S = \text{const}$. It will be noted that in general a Carnot cycle at a temperature $T_2 = 0$ represented by a finite area cannot be plotted on a T-S diagram. In fact, the *isotherm-isentropic curve* $T = 0$, $S = 0$ degenerates into a point on a T-S plane (the origin of coordinates), and at the same time the rectangle, representing the Carnot cycle, degenerates into a segment of the T-axis.

The proved corollary, of course, does not exclude the point $T = 0$ to be approached as close as desired.

11. Thermodynamic Coefficients. Polytropic Processes

By thermodynamic coefficients will be meant expressions of the form $\left(\frac{\partial \gamma}{\partial \mu}\right)_\nu$, where the symbols γ, μ, ν denote the quantities P, V, T, S. The thermodynamic coefficients describe definite properties of a gas: the quantities $\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial V}{\partial T}\right)_S$ are related to the isobaric thermal expansion coefficient of gases α_P and the adiabatic thermal expansion coefficient α_S by formulae

$$\alpha_P = V^{-1}\left(\frac{\partial V}{\partial T}\right)_P, \quad \alpha_S = V^{-1}\left(\frac{\partial V}{\partial T}\right)_S. \tag{11.1}$$

The quantities $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial P}{\partial T}\right)_S$ are related to the isochoric pressure coefficient β_V and the adiabatic pressure coefficient β_S in the following way:

$$\beta_V = P^{-1}\left(\frac{\partial P}{\partial T}\right)_V, \quad \beta_S = P^{-1}\left(\frac{\partial P}{\partial T}\right)_S. \tag{11.2}$$

The quantities $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial V}{\partial P}\right)_S$ are related to the isothermal compressibility K_T and the adiabatic compressibility K_S as follows:

$$K_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T, \quad K_S = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_S. \tag{11.3}$$

The quantities $\left(\frac{\partial S}{\partial T}\right)_V$ and $\left(\frac{\partial S}{\partial T}\right)_P$ are related to the isochoric C_V and the isobaric C_P heat capacities by formulae

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P. \tag{11.4}$$

The quantities $\left(\frac{\partial S}{\partial P}\right)_V = T^{-1}\left(\frac{\delta Q}{\delta P}\right)_V$ and $\left(\frac{\partial S}{\partial P}\right)_T = T^{-1}\left(\frac{\delta Q}{\delta P}\right)_T$ specify the quantity of heat that must be supplied to (or removed from) a gas when pressure is increased by unity, to maintain the volume or temperature constant. Accordingly, the quantities $\left(\frac{\partial S}{\partial V}\right)_P = T^{-1}\left(\frac{\delta Q}{\delta V}\right)_P$ and $\left(\frac{\partial S}{\partial V}\right)_T = T^{-1}\left(\frac{\delta Q}{\delta V}\right)_T$ determine the quantity of heat that must be supplied to a gas upon an increase in volume by unity, so as to maintain the pressure or temperature constant.

Let us arrange the thermodynamic coefficients in an array so that the first line does not contain S, the second P, the third V and the fourth absolute temperature T:

$$\begin{vmatrix} \left(\frac{\partial V}{\partial P}\right)_T & \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial T}{\partial V}\right)_P \\ \left(\frac{\partial S}{\partial T}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S & \left(\frac{\partial V}{\partial S}\right)_T \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial T}{\partial P}\right)_S & \left(\frac{\partial P}{\partial S}\right)_T \\ \left(\frac{\partial V}{\partial P}\right)_S & \left(\frac{\partial P}{\partial S}\right)_V & \left(\frac{\partial S}{\partial V}\right)_P \end{vmatrix} \tag{11.5}$$

We have 12 thermodynamic coefficients. It can be easily shown, however, that only three of them are independent, and the other nine coefficients can be expressed in terms of the three independent coefficients. In fact, it can easily be seen that the product of three coefficients placed in one line of our table is equal to —1. For instance, for the first line of the table

$$\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P = \frac{\partial(V,T)}{\partial(P,T)}\,\frac{\partial(P,V)}{\partial(T,V)}\,\frac{\partial(T,P)}{\partial(V,P)} = -1 \tag{11.6}$$

and, by analogy,

$$\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_S\left(\frac{\partial V}{\partial S}\right)_T = -1, \tag{11.7}$$

$$\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial P}{\partial S}\right)_T = -1, \tag{11.8}$$

$$\left(\frac{\partial V}{\partial P}\right)_S\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_P = -1. \tag{11.9}$$

Five more relationships between thermodynamic coefficients yield the basic thermodynamic identity $\frac{\partial(T, S)}{\partial(P, V)} = 1$. Multiplying both sides of this identity by the Jacobians $\frac{\partial(T, V)}{\partial(T, V)}$, $\frac{\partial(T, P)}{\partial(T, P)}$, $\frac{\partial(S, V)}{\partial(S, V)}$ and $\frac{\partial(S, P)}{\partial(S, P)}$ that are identically equal to unity, and applying the theorem of Jacobians multiplication, we obtain the equalities

$$\frac{\partial(T,S)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(P,V)}=1, \quad \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial T}{\partial P}\right)_V=1, \tag{11.10}$$

$$\frac{\partial(T,S)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(P,V)}=1, \quad \left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial T}{\partial V}\right)_P=-1, \tag{11.11}$$

$$\frac{\partial(T,S)}{\partial(S,V)}\frac{\partial(S,V)}{\partial(P,V)}=1, \quad \left(\frac{\partial T}{\partial V}\right)_S\left(\frac{\partial S}{\partial P}\right)_V=-1, \tag{11.12}$$

$$\frac{\partial(T,S)}{\partial(S,P)}\frac{\partial(S,P)}{\partial(P,V)}=1, \quad \left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial S}{\partial V}\right)_P=1. \tag{11.13}$$

The fifth relationship between thermodynamic coefficients is obtained by expanding the Jacobian

$$\frac{\partial(T,S)}{\partial(P,V)}=\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial V}\right)_P-\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial S}{\partial P}\right)_V=1. \tag{11.14}$$

So we have nine relationships between twelve thermodynamic coefficients.

The three independent thermodynamic coefficients still remain chosen rather arbitrarily—if only the other coefficients were expressed in terms of the three coefficients chosen by means of our nine equations. It is natural, however, that when choosing the three independent thermodynamic coefficients one should be also guided by the following considerations; since as the three remaining coefficients cannot be found within the framework of the thermodynamic method, they must be determined experimentally or from statistical physics.

Let us choose as independent coefficients

$$\left(\frac{\partial V}{\partial P}\right)_T=-K_TV, \quad \left(\frac{\partial P}{\partial T}\right)_V=\beta_VP, \quad \left(\frac{\partial S}{\partial T}\right)_V=\frac{C_V}{T}.$$

These coefficients can be rather easily determined experimentally. As to the possibility of calculating the coefficients, the first two can be calculated directly, if the equation of state of a substance is known; the dependence of the third coefficient on temperature can be found only by the methods of statistical physics. The dependence of C_V on volume, however, can be determined by the thermodynamic method, provided the equation of state is known. Namely, from

Eq. (11.4) we find

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial}{\partial V}\left[\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial V}\right)_T\right]_V$$

$$= T\frac{\partial}{\partial T}\left[\frac{\partial(S,T)}{\partial(V,T)}\right]_V = T\frac{\partial}{\partial T}\left[\frac{\partial(V,P)}{\partial(V,T)}\right]_V = T\frac{\partial^2 P}{\partial T^2}. \qquad (11.15)$$

If pressure is a linear function of temperature, which is true both for an ideal gas, $P = \frac{RT}{V}$, and for a van der Waals gas (see Sec. 12), then $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$ and $C_V = C_V(T)$.

Thus, in addition to the derivation of the equation of state, methods of statistical physics are used to establish the dependence of heat capacity on temperature. Let us separate in the array (11.5) the three chosen coefficients and express through them the remaining coefficients. According to Eq. (11.6), we have

$$\left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial T}{\partial P}\right)_V, \qquad (11.16)$$

and from Eq. (11.10) we find

$$\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial P}\right)_V. \qquad (11.17)$$

Further, on the basis of Eq. (11.11) we obtain

$$\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial T}{\partial P}\right)_V. \qquad (11.18)$$

Now, two coefficients in the second line of the array (11.5) are known, then Eq. (11.7) is used to find the third coefficient

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V, \qquad (11.19)$$

and from Eq. (11.12) we obtain

$$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V. \qquad (11.20)$$

The coefficient $\left(\frac{\partial S}{\partial V}\right)_P$ is found from formula (11.14)

$$\left(\frac{\partial S}{\partial V}\right)_P = \left[1 + \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial S}{\partial P}\right)_V\right]\left(\frac{\partial P}{\partial T}\right)_V$$

$$= \left[1 - \frac{C_V}{T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V^2}\right]\left(\frac{\partial P}{\partial T}\right)_V, \qquad (11.21)$$

and the coefficient $\left(\frac{\partial T}{\partial P}\right)_S$ which is according to formula (11.13) the reciprocal of the above coefficient

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V}{T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2 - C_V}. \tag{11.22}$$

Now two coefficients are known in the third line of the array (11.5), and according to formula (11.8)

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S,$$

whence, using Eq. (11.18), we can write three expressions for the difference in heat capacities, $C_P - C_V$:

$$\begin{aligned} C_P - C_V &= -T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2 = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \\ &= -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2. \end{aligned} \tag{11.23}$$

Since for all substances $\left(\frac{\partial P}{\partial V}\right)_T < 0$ (see Sec. 25), then $C_P > C_V$ (this is obvious for ideal gases, since when heating a gas at $V =$ $=$ const, the supplied heat is spent only to increase the internal energy of the gas, while in the case of isobaric heating the gas performs additional work against external forces).

In thermodynamics, coefficients that are inaccurately measured experimentally have to be expressed in terms of reliably measured coefficients, and not in terms of the three coefficients chosen by us as independent ones. In this case by inaccurately measured coefficients are usually meant all the coefficients containing the entropy S, since the instruments used in experimental physics included all types of manometers, thermometers, etc., but no instruments measuring entropy are available, and the direct measurement of entropy is impossible. So it becomes necessary to "expulse" entropy from the Jacobians. For the solution of this problem the following three rules are formulated.

1. If a Jacobian contains entropy together with temperature, then by virtue of the basic thermodynamic identity

$$\frac{\partial(T, S)}{\partial(\ldots, \ldots)} = \frac{\partial(T, S)}{\partial(P, V)} \frac{\partial(P, V)}{\partial(\ldots, \ldots)} \frac{\partial(P, V)}{\partial(\ldots, \ldots)}.$$

2. If entropy makes up a pair of variables with volume, then

$$\frac{\partial(S, V)}{\partial(\ldots, \ldots)} = \frac{\partial(S, V)}{\partial(T, V)} \frac{\partial(T, V)}{\partial(\ldots, \ldots)} = \frac{C_V}{T} \frac{\partial(T, V)}{\partial(\ldots, \ldots)}.$$

3. If entropy makes up a pair of variables with pressure, then

$$\frac{\partial (S, P)}{\partial (\ldots, \ldots)} = \frac{\partial (S, P)}{\partial (T, P)} \frac{\partial (T, P)}{\partial (\ldots, \ldots)} = \frac{C_P}{T} \frac{\partial (T, P)}{\partial (\ldots, \ldots)}.$$

By way of example calculate the derivative $\left(\frac{\partial T}{\partial P}\right)_S$:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial (T, S)}{\partial (P, S)} = \frac{\partial (T, S)}{\partial (P, V)} \frac{\partial (P, V)}{\partial (P, T)} \frac{\partial (P, T)}{\partial (P, S)} = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P. \quad (11.24)$$

Formula (11.24) has been verified experimentally, in compressing liquids (Joule's experiments). Since the temperature of a liquid undergoing compression changes little even upon rather significant changes in pressure, Eq. (11.24) can be rewritten for finite temperature changes in the form

$$\Delta T_S = \frac{\alpha_P V T}{C_P} \Delta P_S.$$

Joule was one of the first to attempt to verify the validity of the second law of thermodynamics by experimental studies that resulted in a rather good agreement with the theory, taking into account the existing level of experimental techniques.

It will be noted that proceeding from the first law of thermodynamics it is even impossible to determine the direction of an effect. In fact, the internal energy of a liquid undergoing adiabatic compression increases by the amount of work done. However, not knowing the changes in the potential energy of the molecules of the liquid involved, we cannot even predict the change in their kinetic energy and, consequently, in temperature. To solve this problem, we would have to make use of the methods of statistical physics. However, the second law of thermodynamics gives a direct, although formal, answer to the posed question—the sign of $\left(\frac{\partial T}{\partial P}\right)_S$ coincides with the sign of the isobaric expansion coefficient α_P.

It is noteworthy that for water at temperatures below 4 °C the coefficient α_P is negative and, accordingly, the compressed water must undergo cooling in this temperature range, which is fully corroborated by experiments.

We have considered above the calculation of the thermodynamic coefficients, i.e. the derivatives of the form $\left(\frac{\partial \gamma}{\partial \mu}\right)_\nu$, where γ, μ, and ν represent one of the four fundamental thermodynamic quantities P, V, T, S. Thermodynamics also deals sometimes with the calculation of derivatives of the same kind, where the quantities γ, μ, ν or some of them may represent thermodynamic potentials (the internal energy U, free energy F, and also potentials that will be introduced in the following sections). In this case the calculation techniques are somewhat changed, and to express the derivative that is of

interest for us in terms of easily measured quantities, it is necessary to pass over in respective Jacobians to variables that are "natural" for the given thermodynamic potential: when U is involved, to the variables S, V, when dealing with F, to the variables T, V, etc.

Consider by way of example an important problem concerning the dependence of internal energy on volume at $T = \text{const}$. We have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial (U, T)}{\partial (V, T)}.$$

Passing to the variables S, V, we can write

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial (U, T)}{\partial (S, V)} \frac{\partial (S, V)}{\partial (V, T)} = -\left(\frac{\partial S}{\partial T}\right)_V \left[\left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial T}{\partial V}\right)_S - \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial T}{\partial S}\right)_V\right] = -P - T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S$$

and, according to formula (11.19),

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T}\right]. \tag{11.25}$$

The expression on the right-hand side of Eq. (11.25) can be found, if the equation of state of the gas is known.

In particular, for an ideal gas, using the equation of state $PV = RT$, we find

$$\left(\frac{\partial U}{\partial V}\right)_T = 0, \quad U = U(T). \tag{11.26}$$

In order to find the dependence $U(T)$, we note that at constant volume

$$dU_V = \delta Q_V = C_V\, dT, \quad \left(\frac{\partial U}{\partial T}\right)_V = C_V.$$

That is why for an ideal gas

$$U(T) = \int C_V(T)\, dT,$$

and for a perfect gas

$$U(T) = C_V T + \text{const}.$$

From the viewpoint of molecular notions Eq. (11.26) indicates that the molecules of an ideal gas do not interact at a distance (the potential energy of interaction is equal to zero), therefore, the change in molecular spacing does not effect the internal energy, if the average kinetic energy is constant ($T = \text{const}$).

Let us consider in conclusion a process occurring with an arbitrary, but constant heat capacity C—the *polytropic process*. We have

$$\delta Q = C\, dT, \quad dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

whence, according to the energy principle (7.1) and with the account of Eq. (11.25), we have

$$C\,dT = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.$$

It follows that

$$\left(\frac{\partial V}{\partial T}\right)_C = \frac{C - C_V}{T\left(\frac{\partial P}{\partial T}\right)_V}. \tag{11.27}$$

If the thermal equation of state, $P = P(T, V)$, is known, then the relation (11.27) can be integrated, which results in finding the equation of the polytrope in variables T, V; P, V; P, T.

Let us repeat this derivation in greater detail for the particular case of a perfect gas. In this case $P = \frac{RT}{V}$, $C_V = \text{const}$. Equation (11.27) becomes

$$\frac{dT}{T} + (\varkappa - 1)\frac{dV}{V} = 0, \tag{11.28}$$

where the quantity $\varkappa$ is called the *polytropic exponent* and equals

$$\varkappa = \frac{C_P - C}{C_V - C}.$$

Integrating Eq. (11.28), we obtain the equation of the polytrope in variables T, V:

$$TV^{\varkappa - 1} = \text{const},$$

and the equation of state makes it also possible to find the equation of the polytrope in variables P, V:

$$PV^{\varkappa} = \text{const}$$

and in variables P, T:

$$\frac{P^{\varkappa - 1}}{T^{\varkappa}} = \text{const}.$$

Let us consider a number of particular cases.

Isobaric process. We have $C = C_P$, $\varkappa = 0$ and the natural result is

$$P = \text{const}, \quad \frac{V}{T} = \text{const},$$

which represents the Gay-Lussac law.

Isothermal process. In this case $C = \pm\infty$, $\varkappa = 1$ and the trivial result is

$$T = \text{const}, \quad PV = \text{const},$$

which is the mathematical statement of Boyle's law (also known as the Boyle and Mariotte law).

Adiabatic process. In this case $C = 0$, $\varkappa = \gamma = \frac{C_P}{C_V}$ and we have

$$TV^{\gamma-1} = \text{const}, \quad P^{\gamma-1}/T^{\gamma} = \text{const}, \quad PV^{\gamma} = \text{const},$$

which is known as adiabatic law.

Isochoric process. In this case $C = C_V$, $\varkappa \to \pm\infty$; raising the equations of the polytrope to the $\varkappa^{-1}$ power and passing to the limit, we obtain the equalities

$$V = \text{const}, \quad \frac{P}{T} = \text{const}.$$

It should be noted that from the definition of the polytropic exponent it follows that

$$C = \frac{C_P - \varkappa C_V}{1 - \varkappa}. \tag{11.29}$$

Considering the inequalities $C > 0$ and $C < 0$, we find that for positive heat capacities $C > 0$ the values of the polytropic exponent lie in the ranges $-\infty < \varkappa < 1$ and $\gamma < \varkappa < \infty$, and the interval

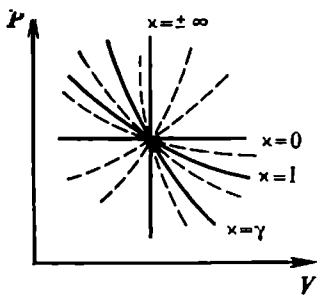


FIG. 16

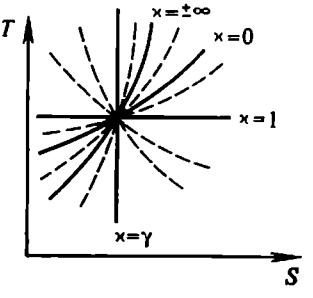


FIG. 17

$1 < \varkappa < \gamma$ corresponds to negative heat capacities, $C < 0$. This means that on the P-V plane the region of polytropic curves passing through a given point and corresponding to the processes characterized by negative heat capacities is located inside the angle formed by an isotherm and an adiabat passing through the same point, as is shown in Fig. 16. This result is absolutely natural, since no heat is supplied to the gas along the adiabat and $C = 0$, and the quantity of heat supplied to the gas along the isotherm is sufficient to compensate for the work done by the gas [for an ideal gas $U = U(T)$ and at $T = \text{const}$ we have $dU = 0$, $\delta Q = \delta A$]. As to the intermediate polytropes, for a gas undergoing expansion, we have $0 < \delta Q < \delta A$ and $dU = \delta Q - \delta A = C_V\, dT < 0$. Hence, $dT < 0$ and $C = \frac{\delta Q}{\delta T} < 0$.

Let us find the equations of polytropic curves plotted on a T-S plane, on which the slope of a polytropic curve is equal to $\left(\frac{\partial T}{\partial S}\right)_C = \frac{T}{C}$, whence, integrating, we find

$$T = T_0 e^{S/C} = T_0 \exp\left[(\varkappa - 1)(\gamma - 1) S/(\varkappa - \gamma) R\right], \quad (11.30)$$

where T_0 is a constant having the dimension of temperature [we used Eq. (11.29) for C and formula $C_V = \frac{R}{\gamma - 1}$]. We have on the T-S plane a set of exponential curves (Fig. 17) that in the particular cases $\varkappa = 0$, $\varkappa = 1$, $\varkappa = \gamma$, $\varkappa \to \pm\infty$ coincide with isobars, isotherms, adiabats and isochores respectively. It is readily seen that for polytropic exponents $\varkappa$ lying in the range $1 < \varkappa < \gamma$, the derivative $\left(\frac{\partial S}{\partial T}\right)_C$ is negative and, consequently, the heat capacity $C = T\left(\frac{\partial S}{\partial T}\right)_C$ is also negative.

Problem

A process is given: (a) in variables (T, V), $\varphi(T, V) = 0$; (b) in variables T, P, $\varphi(T, P) = 0$; (c) in variables (P, V), $\varphi(P, V) = 0$. Find the heat capacity of the gas undergoing these processes. Consider the particular case of a thermally ideal gas.

Answer

(a) $C_\varphi = C_V - T\left(\frac{\partial P}{\partial T}\right)_V \frac{\varphi'_T}{\varphi'_V}$, for ideal gas $C_\varphi = C_V - \frac{P\varphi'_T}{\varphi'_V}$;

(b) $C_\varphi = C_P + T\left(\frac{\partial V}{\partial T}\right)_P \frac{\varphi'_T}{\varphi'_P}$, for ideal gas $C_\varphi = C_P + \frac{V\varphi'_T}{\varphi'_P}$;

(c) $$C_\varphi = \frac{C_V\left(\frac{\partial T}{\partial P}\right)_V \varphi'_V - C_P\left(\frac{\partial T}{\partial V}\right)_P \varphi'_P}{\left(\frac{\partial T}{\partial P}\right)_V \varphi'_V - \left(\frac{\partial T}{\partial V}\right)_P \varphi'_P},$$

for ideal gas $C_\varphi = \frac{VC_V\varphi'_V - PC_P\varphi'_P}{V\varphi'_V - P\varphi'_P}$.

12. Thermodynamics of the van der Waals Gas

As has been already mentioned, real gases obey the equation of state $PV = RT$ but approximately, the more exactly, the higher the temperature of the gas and the smaller its density. At low temperatures and large densities the deviation of real gases from the thermally ideal gas becomes essential. The theoretical derivation of the

equation of state of a real gas cannot be done by methods of phenomenological thermodynamics and falls within the framework of statistical physics (see Sec. 65). Various authors have suggested a vast number of semi-empirical equations of state describing the behaviour of real gases with a greater or smaller degree of accuracy. The simplest and the most applicable of these equations, although not the most accurate, is the van der Waals equation.

The elementary "derivation" of this equation is based on the following qualitative considerations (a more rigorous proof is given in greater detail in Sec. 65).

The concept of a thermally ideal gas implies from the molecular point of view a neglect of the intermolecular forces in a gas. As a matter of fact, the molecules of a real gas interact with one another, and the potential energy of interaction depends on the distance r between the "centres" of the molecules. For the sake of simplicity we consider here molecules as spherically symmetrical formations (actually, it corresponds to the averaging of the "centre" lines of molecules over all directions). The form of the dependence $\mathcal{U}(r)$ is given in Fig. 18. At distances $r < r_0$ intermolecular repulsive forces appearing due to the deformation of electronic shells prevail. These forces increase rapidly as the molecules move closer to one another, and the corresponding branch of the curve $\mathcal{U}(r)$ can be presented with sufficient accuracy by a straight line parallel to the $\mathcal{U}$-axis and extending to infinity (the approximation of hard spheres). At $r > r_0$ the weak attraction forces, appearing between molecules, are owing to the dipole molecular interaction. They decrease at a low rate with increasing intermolecular distance: $\mathcal{U}(r) \propto \propto r^{-6}$. At $r = r_0$ (r_0 can be assumed approximately equal to the molecular "diameter") the repulsion and attraction forces are balanced. The appearing potential well is rather shallow, the order of magnitude of its depth being 10^{-1} to 10^{-2} eV. In cases that are of practical interest, at $T \gtrsim 1$ to 10 K, i.e. above the condensation point, the presence of this well does not lead to the appearance of bound states.

FIG. 18

The indicated properties of the forces of interaction permit the introduction of two corrections into the equation of the state of a thermally ideal gas, $P = \frac{RT}{V}$. The first correction is associated with the molecular repulsion forces. In a hard sphere approximation

each molecule is enclosed by sphere of radius $r_0 = 2\rho_0$, that is "out of the reach" of the centres of other molecules (ρ_0 is the "radius" of a molecule). The volume of this sphere is eight times the molecular volume. Since such a volume is associated with a pair of molecules (the possibility of three or a greater number of molecules drawing closer to each other is ignored, assuming the gas to be rarified), the "inaccessible" volume per one molecule is equal to $4 \cdot \frac{4}{3} \pi \rho_0^3 = 4V_0$. For this reason we replace the volume of the vessel V, present in the equation of the state of an ideal gas, by the volume "free" for molecular motion, $V-b$, where the correction b is equal to $N_A \times 4V_0$, and we obtain the *Clausius equation* for one kilomole,

$$P = \frac{RT}{V-b}, \tag{12.1}$$

from which it follows (as distinguished from the equation $P = \frac{RT}{V}$) that even at $P \to \infty$ the volume of the gas tends not to zero, but to some finite quantity b (Fig. 19).

The second correction is associated with the molecular attraction forces. In the thin surface layer adjoining the wall of a vessel a molecule approaching the wall is acted upon by the field of forces exerted by the remaining molecules. This force field decelerates the molecule and diminishes the strength of blow as the molecule strikes

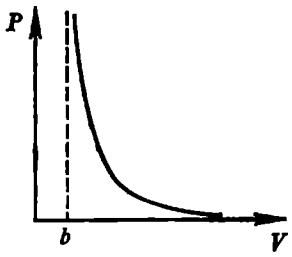


FIG. 19

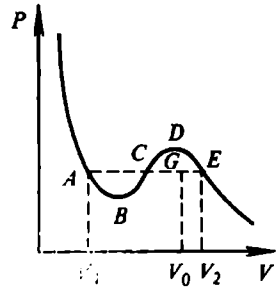


FIG. 20

the wall of the vessel and, consequently, the pressure. The thickness of the layer is of the order of r_0, the range of the molecular interaction forces, and outside of this layer the forces acting upon the molecule are compensated for. Hence we must decrease the pressure determined by Clausius' equation (12.1) by the quantity ΔP that may be assumed proportional to the squared particles density $\left(\frac{N_A}{V}\right)^2$, i.e. inversely proportional to V^2. The reason for this is that the force

acting upon each molecule and the number of molecules striking a unit area of the wall per unit time are proportional to $\frac{N_A}{V}$. The resulting equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{12.2}$$

or

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT, \tag{12.3}$$

is known as *van der Waals' equation* for one kilomole of a gas. The quantities a and b in this equation are constants depending only on the kind of the gas involved.

The attention of the reader should be drawn to the non-strict nature of the foregoing reasonings. It was not proved that the quantities a and b are independent of the temperature and density of a gas. Furthermore, it will be shown in Sec. 65 that a rigorous derivation of the equation of the state of a real gas leads to an infinite series for pressure in powers of V^{-1}, in which only the first coefficients coincide with the expansion coefficients of the expression (12.2). All the same, for a certain range of temperatures and pressures, van der Waals' equation can be used (with some restrictions that will be elucidated below) as a working tool to investigate the thermodynamic properties of gas.

It should be noted for one thing that Eq. (12.3), considered as the equation used to determine the volume when P and T are given, is an equation of the third degree. Upon transformation, this equation takes the following form:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0. \tag{12.4}$$

Since third-dergee equation with real coefficients can have either one real and two complex conjugate roots or three real roots then the straight line plotted on a P-V plane parallel to the V-axis may cross an isotherm either at three points or at one. A van der Waals' isotherm plotted at not very high temperatures is shown in Fig. 20. The left, steeply falling branch of the curve corresponds to the liquid state of a substance, and the right flat branch—to the gaseous state. The transition from the liquid state to the gaseous state and back occurs under ordinary conditions not along the van der Waals isotherm $ABCDE$, but along the isobar AE (represented by the dotted line) which is simultaneously a real isotherm. As will be shown in Sec. 26, the location of the isobar is determined by the equality of the areas ABC and CDE—by Maxwell's equal area rule.

The points on the isobar-isotherm AE represent two-phase states of a substance. The closer the representing point to A, the more

there is liquid in the system, and the closer the point to E, the more there is vapour in the system. If we denote the maximum volume of a mole of liquid and the minimum volume of a mole of vapour at temperature T by V_1 and V_2 respectively, and the volume of the two-phase system at point G by V_0 (Fig. 20), then $V_0 = xV_1 + (1 - x) V_2$, where x is the fraction of liquid in the state G. Whence follow the relationships

$$x = \frac{V_2 - V_0}{V_2 - V_1}, \quad \frac{x}{1-x} = \frac{V_2 - V_0}{V_0 - V_1}, \tag{12.5}$$

called (by analogy with mechanics) the *lever rule*.

The branches AB and DE of the van der Waals isotherm represent metastable states of substance: supercooled liquid and supersaturated vapour, and these states can be realized under certain conditions. The section BCD, on which $\left(\frac{\partial P}{\partial V}\right)_T > 0$, corresponds to absolutely unstable states of substance and can never be realized (see Sec. 27).

The fact that van der Waals' equation leads to such states demonstrates once more the restricted application of the equation. At sufficiently low temperatures the section of the isotherm pertaining to the liquid state may run below the V-axis. Such metastable states of liquid at a negative pressure (stretched liquid) may actually be observed in experimental studies. With rising temperature the branch of van der Waals' isotherm where humps and valleys are observed diminishes (Fig. 21) and at a temperature T_{cr}—*critical temperature*—it turns into a point of inflection with a horizontal tangent. At this point (*critical point*) we have

$$\left(\frac{\partial P}{\partial V}\right)_{cr} = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{cr} = 0. \tag{12.6}$$

Equations (12.2) and (12.6) can be used to find all the three parameters of the critical point, that is critical temperature T_{cr}, critical pressure P_{cr} and critical volume V_{cr}.

Use can also be made of the fact that at the critical point the three roots of third-degree equation (12.4) merge into one, so that in the neighbourhood of the critical point this equation takes the form

$$(V - V_{cr})^3 = V^3 - 3V_{cr}V^2 + 3V_{cr}^2 V - V_{cr}^3. \tag{12.7}$$

Equating the coefficients in Eqs. (12.7) and (12.4), we obtain a system of equations

$$V_{cr}^3 = \frac{ab}{P_{cr}}, \quad V_c^2 = \frac{a}{P_{cr}}, \quad 3V_{cr} = b + \frac{RT_{cr}}{P_{cr}}$$

solving this system of equations we find

$$T_{cr} = \frac{8a}{27Rb}, \quad R_{cr} = \frac{a}{27b^2}, \quad V_{cr} = 3b. \tag{12.8}$$

Let us replace the pressure, volume and temperature by the dimensionless parameters $\tilde{P} = P/P_{cr}$, $\tilde{V} = V/V_{cr}$ and $\tilde{T} = T/T_{cr}$— the reduced pressure, volume and temperature. Then, van der Waals' equation becomes

$$\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T}, \tag{12.9}$$

from which all the individual parameters of gas, the constants a and b, are eliminated. This result is a particular case of the more general statement—the *law of corresponding states*, according to which

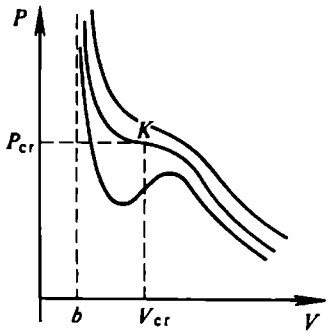


FIG. 21

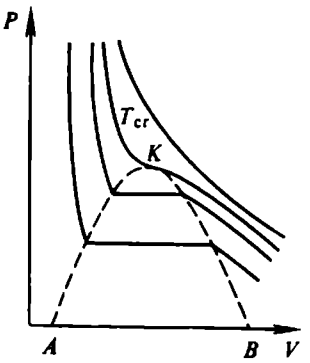


FIG. 22

for all gases with two equal values of the three reduced parameters of state ($\tilde{P}$, $\tilde{V}$ and $\tilde{T}$), the values of third reduced parameters also happen to be the same automatically. When formulated in such a general way, not associated with a particular form of Eq. (12.9), the law of corresponding states is in a far more exact agreement with experimental results than the van der Waals equation.

Let us plot on a P-V plane a set of van der Waals' isotherms corrected in accordance with the Maxwell equal area rule (Fig. 22) (the region of humps and valleys is replaced by an isobar). The curves connecting the initial and final points of the isobars converge at the critical point and divide the P-V plane into three regions. The region bounded by the curve AK and the upper part of the critical isotherm represents the liquid-state region. The region located inside the dome-shaped curve AKB (referred to as the coexistence curve) describes two-phase states (liquid and saturated vapour). The two-phase state is impossible in the region located above the critical isotherm and to the right of the curve BK and with increasing temperature and volume the isotherms become close (in the form) to the isotherms of an ideal gas, for which PV = const. Consequently,

the following physical meaning can be attributed to the critical parameters P_{cr}, V_{cr}, T_{cr}. The critical pressure is the maximum pressure of a saturated vapour, the critical volume is the maximum (molar) volume of a liquid, and the critical temperature is the minimum temperature at which any substance can exist in a liquid state. As the critical point is approached, the difference between the molar volumes of vapour and liquid $V_2 - V_1$ diminishes, and the difference vanishes at the critical state. This means that at the critical point the difference in the physical properties of a liquid and a vapour vanishes.

We shall turn again to the behaviour of a gas in the neighbourhood of the critical point in Chapter VIII, devoted to the statistical theory of phase transitions. Let us pass now to the thermodynamic relationships and find the basic thermodynamic functions of the van der Waals gas and first of all, its entropy. According to Eq. (11.17)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV,$$

whence with the aid of (12.2) we find

$$dS = \frac{C_V}{T} dT + \frac{R}{V-b} dV. \tag{12.10}$$

It was already shown in the preceding section that for a van der Waals gas the heat capacity C_V is independent of the volume: $C_V = C_V(T)$. Therefore, the two terms in Eq. (12.10) are total differentials and by integrating it we obtain

$$S = \int \frac{C_V(T)}{T} dT + R \ln (V-b) + \text{const}. \tag{12.11}$$

If we consider $C_V = \text{const}$, which can be assumed in a rather wide temperature range, then

$$S - S_0 = C_V \ln \left(\frac{T}{T_0}\right) + R \ln \left(\frac{V-b}{V_0-b}\right). \tag{12.12}$$

Passing to the variables P, V and using van der Waals' equation, we derive two other formulae for S:

$$\begin{aligned} S - S_0 &= C_V \ln \frac{P + \frac{a}{V^2}}{P_0 + \frac{a}{V_0^2}} + C_P \ln \frac{V-b}{V_0-b}, \\ S - S_0 &= C_P \ln \frac{T}{T_0} - R \ln \frac{P + \frac{a}{V^2}}{P_0 + \frac{a}{V_0^2}}. \end{aligned} \tag{12.13}$$

The volume can be eliminated from Eq. (12.12) or Eq. (12.13) and the entropy can be presented as a function of T and P only by solving

the cubic equation (12.4), which leads to extremely cumbersome formulae.

Let us find the internal energy of a van der Waals' gas. Equations (12.12) and (12.10) are used to obtain

$$dU = T\,dS - P\,dV = C_V\,dT + \frac{a}{V^2}\,dV.$$

Upon integration we find

$$U = \int C_V(T)\,dT - \frac{a}{V} + \text{const} \tag{12.14}$$

and at $C_V = \text{const}$

$$U - U_0 = C_V(T - T_0) - \frac{a}{V} + \frac{a}{V_0}. \tag{12.15}$$

The internal energy can readily be expressed as a function of the natural variables S, V. Eliminating temperature from Eq. (12.15), we use formula (12.12) to find

$$U - U_0 = C_V T_0 \left[e^{\frac{S-S_0}{C_V}R} \left(\frac{V_0 - b}{V - b} \right)^{\frac{R}{C_V}} - 1 \right] - \frac{a}{V} + \frac{a}{V_0}. \tag{12.16}$$

Calculate also the difference $C_P - C_V$ for a van der Waals gas. According to formula (11.23), we have

$$C_P - C_V = T \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_P}.$$

and, finding by formula (12.2) the respective derivatives, we obtain

$$C_P - C_V = R \frac{P + \frac{a}{V^2}}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}.$$

Assuming that $\frac{a}{V^2} \ll P$, $b \ll V$ and retaining only infinitesimals of the first order of magnitude, we find

$$C_P - C_V \approx R\left(1 + \frac{2a}{PV^2}\right) \approx R\left(1 + \frac{2a}{RTV}\right). \tag{12.17}$$

Let us find now the variation of the temperature of the adiabatically expanding gas, depending on pressure. According to formulae (12.2) and (11.24), we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{C_P\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)} \approx \frac{RT}{PC_P}\left(1 + \frac{a}{PV^2}\right). \tag{12.18}$$

Since the right-hand side of Eq. (12.18) is positive, then $\left(\frac{\partial T}{\partial P}\right)_S > 0$, and with decreasing pressure (expansion of the gas) gas temperature drops, with this decrease in temperature occurring at a higher rate than for an ideal gas.

We shall point out in concluding this section (without a detailed analysis) some other equations of state used to describe real gases.

The first Dieterici equation

$$P(V-b) = RTe^{-a/RTV}. \tag{12.19}$$

The second Dieterici equation

$$\left(P + \frac{a}{V^{5/3}}\right)(V-b) = RT. \tag{12.20}$$

The Berthelot equation

$$\left(P + \frac{a}{V^2T}\right)(V-b) = RT. \tag{12.21}$$

The Kamerlingh Onnes equation (or virial expansion, see Sec. 65)

$$PV = RT\left(1 + \frac{A_2}{V} + \frac{A_3}{V^2} + \ldots\right). \tag{12.22}$$

The quantities A_i are called the *virial coefficients* and expressed by formulae of the kind

$$A_i = b_{i1} + \frac{b_{i2}}{T} + \frac{b_{i3}}{T^2} + \ldots.$$

Problems

1. Find the free energy of the van der Waals gas.

Answer. $F - F_0 = C_V(T - T_0) - C_V T \ln\left(\frac{T}{T_0}\right) - RT \ln\frac{V-b}{V_0-b}$.

2. Find the work done upon isothermal expansion of the van der Waals gas from volume V_1 to volume V_2.

Answer. $A_T = RT \ln\frac{V_2-b}{V_1-b} + \frac{a}{V_2} - \frac{a}{V_1}$.

3. Find the quantity of heat that must be supplied to 1 kilomole of the van der Waals gas upon an increase of its volume by unity, so that the temperature of the gas would remain constant.

Answer. $\left(\frac{\delta Q}{\delta V}\right)_T = \frac{RT}{V-b}$.

4. Find the critical parameters and write down in dimensionless variables $\tilde{P}$, $\tilde{V}$, $\tilde{T}$ the equation of state of a gas obeying:

(a) the first Dieterici equation; (b) the second Dieterici equation; (c) the Berthelot equation.

Answer. (a) $P_{cr}=\frac{a}{4b^2e^2}$, $V_{cr}=2b$, $T_{cr}=\frac{a}{4Rb}$,

$$\tilde{P}=\frac{\tilde{T}}{2\tilde{V}-1}\exp\frac{2(\tilde{V}\tilde{T}-1)}{\tilde{V}\tilde{T}};$$

(b) $P_{cr}=\frac{a}{2^{16/3}b^{5/3}}$, $V_{cr}=4b$, $T_{cr}=\frac{15}{2^{16/3}}\frac{a}{Rb^{2/3}}$,

$$\tilde{P}=\frac{15\tilde{T}}{4\tilde{V}-1}-\frac{4}{\tilde{V}^{5/3}};$$

(c) $P_{cr}=\left(\frac{aR}{216b^3}\right)^{1/2}$, $V_{cr}=3b$, $T_{cr}=\left(\frac{8a}{27Rb}\right)^{1/2}$,

$$\tilde{P}=\frac{8\tilde{T}}{3\tilde{V}-1}-\frac{3}{\tilde{V}^2\tilde{T}}.$$

13. Gas Cooling Methods. Gay-Lussac and Joule-Thomson Processes

As can be seen from formula (12.18), reversible adiabatic expansion of a gas can be used to cool it. However, slow reversible expansion of a gas, realized adiabatically, fails to be a technically convenient method for obtaining low temperatures. Let us consider in this connection two more experiments.

The first of these experiments was carried out by Gay-Lussac, using the set-up shown schematically in Fig. 23. After valve B is opened, the gas rushes from vessel A into vessel C that was evacuated beforehand, the experiment being conducted under conditions of ideal heat insulation. Upon the elapse of some time (greater than the pressure relaxation time but smaller than the characteristic time of heat conduction through the heat-insulating walls) thermal equilibrium sets in in the vessels, and the change in temperature, T_2-T_1, can be measured. Gay-Lussac's experiment has shown that $T_2=T_1$ (within the experiment's error limits). As can easily be seen, it follows from these results that the internal energy does not depend on volume. In fact, inasmuch as Gay-Lussac's process occurs adiabatically without performing work against external forces (the gas expands into an evacuated space), the internal energy remains constant

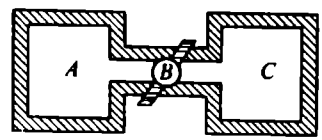


FIG. 23

$$U(V_1, T_1)=U(V_2, T_2).$$

Since $T_1 = T_2$, from this it follows, that the internal energy is independent of volume. Let us see what temperature changes take place when the Gay-Lussac process occurs in a real gas. It should be noted in the first place that this process is an irreversible adiabatic process and, strictly speaking, it does not fall within the framework of the ideas developed so far. In particular, we cannot claim that the entropy remains constant in the Gay-Lussac process: as will be shown in Sec. 23, the entropy increases in irreversible adiabatic processes. We can, however, widen the scope of problems being solved by us, including the Gay-Lussac process with the aid of the reasoning often employed in thermodynamics.

Inasmuch as we are concerned only with the final equilibrium state of the gas after its expansion to volume V_2, let us replace mentally the Gay-Lussac process by an imaginary reversible process leading to the same final state. We can visualize this process as an infinitely slow expansion of the gas to volume V_2, proceeding at a constant internal energy U. This imaginary process, of course, will be neither adiabatic, nor isentropic. On the contrary, as we shall see in Sec. 23, the process must be realized with a certain quantity of heat being supplied to the gas.

Since we are interested in the change in the temperature of the gas undergoing the Gay-Lussac process (this change will evidently be the same as in the imaginary isentropic process), let us find the derivative $\left(\frac{\partial T}{\partial V}\right)_U$. Passing over to the "natural" variables of internal energy, S and V, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{\partial (T, U)}{\partial (V, U)} = \frac{\partial (T, U)}{\partial (V, S)} \frac{\partial (V, S)}{\partial (V, U)}$$

$$= \frac{1}{T}\left[T\left(\frac{\partial T}{\partial V}\right)_S + P\left(\frac{\partial T}{\partial S}\right)_V\right]. \quad (13.1)$$

Using formula (11.19), we finally obtain

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{T}{C_V}\left[\frac{P}{T} - \left(\frac{\partial P}{\partial T}\right)_V\right]. \quad (13.2)$$

It will readily be seen that for an ideal gas this expression vanishes.

For a real gas, however, using van der Waals' equation as a model, we find

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{V^2 C_V}.$$

One can see from the above formula that when the Gay-Lussac process is realized with a real gas, it slightly cools, since the correction a/V^2 in van der Waals' equation is small compared with pressure P, and the decrease in temperature, $\frac{a}{V^2 C_V}\Delta V$, is small compared with T. For this reason such small temperature variations could not be

observed in Gay-Lussac's experiments involving great errors (since the heat capacity of the walls of the vessel is large compared with the heat capacity of the gas).

In this connection, Joule and Thomson carried out an experiment permitting far more exact measurements. Before presenting a description of the Joule-Thomson experiment, we have to introduce one more thermodynamic function in addition to the adiabatic potential, internal energy U, and the isothermal potential, free energy F. This new function referred to as *heat content*, or *enthalpy*, is specified by formula

$$W = U + PV. \tag{13.3}$$

The differential of this function is

$$dW = dU + P\,dV + V\,dP,$$

or

$$dW = T\,dS + V\,dP, \tag{13.4}$$

and the natural variables of W are S and P. The derivatives of enthalpy with respect to these variables are

$$\left(\frac{\partial W}{\partial S}\right)_P = T, \quad \left(\frac{\partial W}{\partial P}\right)_S = V. \tag{13.5}$$

Let us consider now the so-called *Joule-Thomson process*. An idealized schematic diagram of the experiment is shown in Fig. 24. The gas filling a heat-insulated tube is forced through a porous partition with the aid of a piston. Constant pressures P_1 and P_2 ($P_1 > P_2$) are maintained to the left and to the right of the partition with the aid of pistons, so that the entire process is a steady-state one. (In practice the Joule-Thomson process is realized in a somewhat different manner, the role of the pistons being played by a compressor, creating a pressure drop and a steady-state gas flow, and the role of the porous partition being played by a valve.)

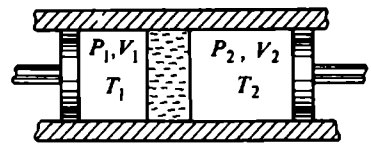


FIG. 24

Let us prove that the Joule-Thomson process occurs at a constant heat content (enthalpy), i.e. it is an isoenthalpic process. Let a certain quantity of gas, occupying to the left of the partition volume V_1, occupy, after being forced through the porous plug, volume V_2 to the right of it. The change in the internal energy of the gas, $U_2 - U_1$, is equal to the work done on the gas, $P_1V_1 - P_2V_2$, whence

$$U_2 - U_1 = P_1V_1 - P_2V_2, \quad W_2 = W_1. \tag{13.6}$$

Attention should be paid to the fact that just as the Gay-Lussac process, the Joule-Thomson process is an irreversible adiabatic process. Using the same reasoning as in the case of the Gay-Lussac process, let us replace the Joule-Thomson process by an imaginary isoenthalpic process, proceeding from the same initial state P_1, V_1, T_1 to the same final state P_2, V_2, T_2 as the real Joule-Thomson process.

Since we are interested in the change in the gas temperature in the Joule-Thomson process (this change will evidently be the same as in the imaginary isoenthalpic process), let us find the derivative $\left(\frac{\partial T}{\partial P}\right)_W$. Passing over for W to the natural variables, S, P, we have

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{\partial (T, W)}{\partial (P, W)} = \frac{\partial (T, W)}{\partial (P, S)} \frac{\partial (P, S)}{\partial (P, W)}$$
$$= \frac{1}{T}\left[\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial W}{\partial S}\right)_P - \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial W}{\partial P}\right)_S\right].$$

By virtue of the equality $dW = T\,dS + V\,dP$, we find

$$\left(\frac{\partial T}{\partial P}\right)_W = \left(\frac{\partial T}{\partial P}\right)_S - \frac{V}{C_P}.$$

Using formula (11.24), we finally get

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{T}{C_P}\left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{V}{T}\right]. \tag{13.7}$$

For an ideal gas we obtain $\left(\frac{\partial T}{\partial P}\right)_W = 0$, i.e. the Joule-Thomson effect does not occur.

To investigate formula (13.7) as applied to real gases, let us pass over in the right-hand side to the variables T, V, using the relation

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial (V, P)}{\partial (T, P)} = \frac{\partial (V, P)}{\partial (V, T)} \frac{\partial (V, T)}{\partial (T, P)} = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T;$$

then we obtain

$$\left(\frac{\partial T}{\partial P}\right)_W = -\left[V\left(\frac{\partial P}{\partial V}\right)_T + T\left(\frac{\partial P}{\partial V}\right)_V\right] \frac{1}{C_P}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\lambda\left(\frac{\partial V}{\partial P}\right)_T}{C_P}. \tag{13.8}$$

Since $\left(\frac{\partial P}{\partial V}\right)_T < 0$, the sign of the derivative $\left(\frac{\partial T}{\partial P}\right)_W$ coincides with that of $\lambda = V\left(\frac{\partial P}{\partial V}\right)_T + T\left(\frac{\partial P}{\partial T}\right)_V$.

Let us examine the behaviour of a gas obeing van der Waals' equation. In this case

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \quad \left(\frac{\partial P}{\partial V}\right)_T = \frac{2a}{V^3} - \frac{RT}{(V-b)^2}$$

and

$$\lambda = \frac{2a}{V^2} - \frac{RTb}{(V-b)^2}. \tag{13.9}$$

At $\lambda < 0$ the Joule-Thomson effect is negative, that is, the permeation of the gas through the porous plug is accompanied by heating, at $\lambda > 0$ the effect is positive—the gas is cooled, and at $\lambda = 0$ we have the so-called inversion point (at which the effect changes its sign). The inversion points are determined by equation

$$\lambda = \frac{2a}{V^2} - \frac{RT_i b}{(V-b)^2} = 0. \tag{13.10}$$

Since we are interested in the inversion temperature as a function of pressure, we eliminate volume from Eq. (13.10) by means of van der Waals' equation to find

$$\frac{V-b}{V} = \sqrt{\frac{RT_i b}{2a}}.$$

Introducing the notation $\sqrt{\frac{RT_i b}{2a}} = x$, we find

$$V = \frac{b}{1-x}, \quad V-b = \frac{bx}{1-x}. \tag{13.11}$$

Substituting this into van der Waals' equation, we obtain for x the quadratic equation

$$x^2 - \frac{4}{3}x + \frac{1}{3}\left(1 + \frac{Pb^2}{a}\right) = 0, \tag{13.12}$$

whence

$$x = \frac{2}{3}\left[1 \pm \frac{1}{2}\sqrt{1 - \frac{3Pb^2}{a}}\right], \tag{13.13}$$

and the inversion temperature is

$$T_i = \frac{8a}{9Rb}\left[1 \pm \frac{1}{2}\sqrt{1 - \frac{3Pb^2}{a}}\right]^2.$$

Introducing the critical temperature $T_{cr} = \frac{8a}{27Rb}$ and the critical pressure $P_{cr} = \frac{a}{27b^2}$, we rewrite the last formula in the form

$$T_i = 3T_{cr}\left[1 \pm \frac{1}{2}\sqrt{1 - \frac{P}{9P_{cr}}}\right]^2. \tag{13.14}$$

It can be seen that two points of inversion exist at $P < 9P_{cr}$: the upper $\bar{T}_i$ and the lower $\underline{T}_i$, the difference between which diminishes with rising pressure; at $P = 9P_{cr}$ the two points of inversion merge into one point $T_i' = 3T_{cr}$. On the contrary, at $P \to 0$, $\bar{T}_i \to \frac{27}{4}T_{cr}$; $\underline{T}_i \to \frac{3}{4}T_{cr}$. For most gases at low pressures the lower inversion

point is located in the liquid-state region. The inversion curve plotted on a P-T plane is dome-shaped as shown in Fig. 25. The region of the positive effect lies inside the curve. This is evident, if only from the fact that according to formula (13.9) λ becomes negative when $T \to \infty$ and volume V is fixed.

For most gases (with the exception of hydrogen and helium) the upper inversion temperatures are high compared to room temperature, and for these gases $\lambda > 0$ even at room temperature. It follows that the Joule-Thomson effect results in a decrease in gas temperature and its use in nitrogen liquefaction plants is associated with this property of the effect.

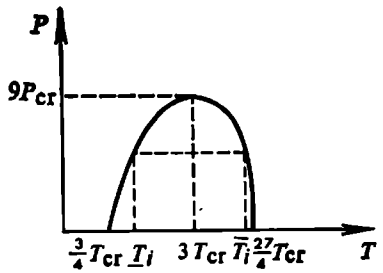


FIG. 25

For H_2 and He, used under ordinary pressures, the upper inversion temperatures are very low, and at room temperature the Joule-Thomson process results in the heating of the gas. In this connection, for hydrogen and helium to be liquefied, they must first be cooled using other methods, below the inversion temperature. Hydrogen is cooled by bringing the gas into contact with liquid air, and helium with liquid hydrogen.

As is seen from expression (13.9), the positive effect takes place when the correction a/V^2 in van der Waals' equation is of primary importance, and the negative effect when the correction b prevails. This can be easily understood, using the ideas of molecular theory. The correction $\frac{a}{V^2}$ is associated with the action of molecular attraction forces, and when these forces prevail they decelerate the motion of molecules as they move apart—when the gas expands after forcing its way through the porous plug. In this case the kinetic energy of the molecules and, consequently, the gas temperature decrease. The correction b is associated with the finite volume of the molecules, i.e. with the action of the molecular repulsion forces as the molecules draw closer. If these forces prevail, they accelerate the molecules as they move apart, with the kinetic energy of the molecules and gas temperature therefore increasing.

So far we have been considering the differential Joule-Thomson effect manifesting itself during infinitely small drops in pressure Of practical interest is the integral effect, for which

$$T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_W dP. \tag{13.15}$$

In practical applications the value of T_1 is determined by the choice of method for precooling the gas, and the magnitude of P_2 coincides approximately with atmospheric pressure. Let us find what initial pressure P_1 must be chosen for the effect to be maximum. Differentiating Eq. (13.15) with respect to P_1, we find that $\left(\frac{\partial T_2}{\partial P}\right)_W = 0$ at $P = P_1$, $T = T_1$. But this is the condition under which the initial state lies on the inversion curve for the differential Joule-Thomson effect; consequently, having chosen the precooling temperature T_1, we can find the optimal initial pressure on the inversion curve.

It should be noted in conclusion that all the results obtained agree only qualitatively with experiment, since van der Waals' equation describes only approximately the behaviour of real gases.

Problem

Find the equation of the inversion curve in variables $\tilde{P}$, $\tilde{T}$ for (a) the first Dieterici equation, (b) for the Berthelot equation.

Answer. (a) $\tilde{P} = 8\left(1 - \frac{1}{8}\tilde{T}\right)\exp\left(\frac{5}{2} - \frac{4}{\tilde{T}}\right)$;

(b) $\tilde{P} = 18\sqrt{2}\left(1 - \frac{2\sqrt{2}}{9}\tilde{T}\right) - \frac{27}{\tilde{T}}\left(1 - \frac{2\sqrt{2}}{9}\tilde{T}\right)^2$.

14. Thermodynamics of Rods

Let us turn now from the thermodynamic properties of homogeneous systems, described by parameters P, V, to the treatment of other thermodynamic systems.

By way of example let us first examine a rod having a length l and acted upon by a longitudinal tensile force f. The work done as the rod is stretched by dl is expressed, in accordance with the selected rule of signs, by formula

$$\delta A = -f\,dl. \tag{14.1}$$

Comparing this with the formula of work derived for gases, $\delta A = P\,dV$, it can be seen that in order to pass from relations of the thermodynamics of gases to relations of the thermodynamics of rods, the following substitutions must be made:

$$P \to -f, \quad V \to l, \tag{14.2}$$

Thus, in the thermodynamics of rods the role of the generalized force is played by the quantity $-f$, and the role of the generalized coordinate by the length of the rod l. The basic thermodynamic equation then takes on the appearance

$$dU(S, l) = T\,dS + f\,dl \tag{14.3}$$

or, by means of the Jacobian,

$$\frac{\partial (T, S)}{\partial (f, l)} = -1. \tag{14.4}$$

In the thermodynamics of rods the equation of state, expressed in the form $P = P(V, T)$ for gases, will evidently take the form $f = f(l, T)$. In cases of large strains (deformations) and a wide range of temperatures the exlicit form of this equation is rather complex and it can be found only by experiment. However, over quite a wide range of temperatures not close to the fusing point, the length of a rod as a function of temperature and the tensile force, $l(T, f)$, will be expressed by formula

$$l(T, 0) = l(T_0, 0)[1 + \alpha (T - T_0)], \tag{14.5}$$

where $T_0 = 273.15$ K, α is coefficient of linear expansion, depending only on the material of the rod, not on its length and temperature, and according to Hooke's law

$$\frac{l(T, f) - l(T, 0)}{l(T, 0)} = \frac{1}{E\sigma} f, \tag{14.6}$$

where E = Young's modulus, depending on the material of the rod and weakly depending on temperature;
σ = cross-sectional area of the rod.

Combining relationships (14.5) and (14.6), we obtain the equation of state for an ideal rod:

$$f = E\sigma \left\{ \frac{l}{l_0 [1 + \alpha (T - T_0)]} - 1 \right\}, \tag{14.7}$$

where $l_0 = l(T_0, 0)$.

Below, the quantities E and α will be taken as constant for an "ideal" rod, and we shall ignore the change in the cross-sectional area σ upon extension (an allowance for this change yields effects of the second order of magnitude with respect to relative deformation $\Delta l/l$). Since for most solids the coefficient of linear expansion $\alpha \sim 10^{-5}$ deg^{-1}, the product $\alpha (T - T_0)$ remains rather small compared to unity up to temperatures close to fusing point; thus quantities of the second order of magnitude with respect to αT will be ignored. In particular, within the accuracy limits indicated, formula (14.7) can be rewritten in the form

$$f = E\sigma \left\{ \frac{l}{l_0} [1 - \alpha (T - T_0)] - 1 \right\}. \tag{14.8}$$

Only formula (14.8) will be used below as the equation of state of a rod.

The isotherms of an ideal rod plotted on the f-l plane are shown in Fig. 26. The dotted segments of the curves are isotherms outside

the region of elastic deformation, where Young's modulus becomes dependent on deformation and decreases compared to its magnitude in the elastic region.

Let us now find the most important thermodynamic functions of the ideal rod, above all its entropy, making use for this purpose of the formula $\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_l$, obtained from formula (11.17) upon the standard substitution (14.2). Then

$$dS = \left(\frac{\partial S}{\partial T}\right)_l dT + \left(\frac{\partial S}{\partial l}\right)_T dl = \frac{C_l}{T} dT - \left(\frac{\partial f}{\partial T}\right)_l dl. \qquad (14.9)$$

From the equation of state (14.8) we find

$$\left(\frac{\partial f}{\partial T}\right)_l = -\frac{\alpha E \sigma l}{l_0}$$

whence

$$dS = \frac{C_l}{T} dT + \frac{\alpha E \sigma l}{l_0} dl. \qquad (14.10)$$

In order to integrate the above equation, the dependence of C_l on T and l must be known. In spite of the fact that we are considering rods—thermodynamic objects differing in their nature both from ideal and real gases, there exists an important, even if formal, similarity between the equations of state in these three cases—ideal gases, real gases, and ideal rods. This similarity is that in all three cases the generalized force (P for gases, f for rods) is a linear function of temperature [Eq. (14.8)]. It follows from this that for an ideal rod C_l is independent of l, just as for ideal and real gases C_V is independent of V.

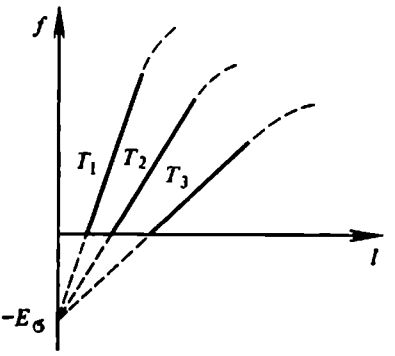


FIG. 26

This assertion can be proved by substitution $P \to -f$, $V \to$ in formula (11.15):

$$\left(\frac{\partial C_l}{\partial l}\right)_T = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_l = 0.$$

Integrating now the equation (14.10), we find

$$S = \int \frac{C_l(T)\, dT}{T} + \frac{\alpha E \sigma l^2}{2 l_0} + \text{const}. \qquad (14.11)$$

The dependence of C_l on temperature, just as that of C_V for gases, cannot be found within the framework of thermodynamics, and is

specified in statistical physics. It will be shown in Sec. 53 that for a number of bodies at not very low temperatures C_l is constant and amounts to about 2.5×10^4 J/deg·kmol (Dulong and Petit law). For such (perfect) rods formula (14.11) takes the form

$$S = C_l \ln T + \frac{\alpha E \sigma l^2}{2l_0} + \text{const}. \tag{14.12}$$

Let us find the expression for the internal energy of an ideal rod. According to (14.10) and (14.8),

$$dU = T\,dS + f\,dl = C_l\,dT + \left(\alpha E \sigma T \frac{l}{l_0} + f\right) dl \approx C_l\,dT + E\sigma \frac{l - l_0}{l_0}\,dl$$

and

$$U = \int C_l(T)\,dT + \frac{E\sigma (l - l_0)^2}{2l_0} + \text{const}, \tag{14.13}$$

and for perfect rods

$$U = C_l T + \frac{E\sigma (l - l_0)^2}{2l_0} + \text{const}. \tag{14.14}$$

In contrast to ideal gases, whose energy is independent of volume, the energy of ideal rods is a quadratic function of deformation.

Like the array of thermodynamic coefficients of gases (11.5), the thermodynamic coefficients of rods can be set out as follows:

$$\begin{vmatrix} \left(\frac{\partial l}{\partial T}\right)_f & \left(\frac{\partial f}{\partial l}\right)_T & \left(\frac{\partial T}{\partial f}\right)_l \\ \left(\frac{\partial S}{\partial T}\right)_f & \left(\frac{\partial f}{\partial S}\right)_T & \left(\frac{\partial T}{\partial f}\right)_S \\ \left(\frac{\partial S}{\partial T}\right)_l & \left(\frac{\partial l}{\partial S}\right)_T & \left(\frac{\partial T}{\partial l}\right)_S \\ \left(\frac{\partial S}{\partial l}\right)_f & \left(\frac{\partial f}{\partial S}\right)_l & \left(\frac{\partial l}{\partial f}\right)_S \end{vmatrix}. \tag{14.15}$$

As with gases, only three of these coefficients are independent. In the thermodynamics of rods it is best to choose as the basic three coefficients $\left(\frac{\partial l}{\partial T}\right)_f$, $\left(\frac{\partial f}{\partial l}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_f = \frac{C_f}{T}$. The first two can be readily measured on the one hand, while they are specified by the equation of state of rods on the other. In particular, for ideal rods we have

$$\left(\frac{\partial l}{\partial T}\right)_f = \alpha l_0, \tag{14.16}$$

$$\left(\frac{\partial f}{\partial l}\right)_T = \frac{E\sigma}{l_0}\left[1 - \alpha (T - T_0)\right] \approx \frac{E\sigma}{l_0}. \tag{14.17}$$

For rods it is easier to measure the heat capacity C_f than C_l. Let us find the difference $C_f - C_l$ for ideal rods. Carrying out the

standard substitution (14.2) in formula (11.23), we obtain

$$C_f - C_l = T\left(\frac{\partial f}{\partial l}\right)_T \left(\frac{\partial l}{\partial T}\right)_f^2. \tag{14.18}$$

Substituting (14.16) and (14.17) into Eq. (14.18), we find

$$C_f - C_l = (\alpha T)^2 \frac{E\sigma l_l}{T}, \tag{14.19}$$

and since the right-hand side of Eq. (14.19) is the second-order infinitesimal in αT, the difference $C_f - C_l$ is very small and can be taken as equal to zero for the degree of approximation assumed.

Let us express by way of example the coefficient $\left(\frac{\partial T}{\partial f}\right)_S$, characterizing the change in temperature upon adiabatic extension of a rod, in terms of easily measured quantities. Making use of formula (11.24) and carrying out the standard substitution (14.2), we get

$$\left(\frac{\partial T}{\partial f}\right)_S = -\frac{T}{C_f}\left(\frac{\partial l}{\partial T}\right)_f \approx -\frac{\alpha l_0 T}{C_f}. \tag{14.20}$$

Since for most solids $\alpha > 0$, then $\left(\frac{\partial T}{\partial f}\right)_S < 0$, i.e. rods cool with an increase in load. Experimental studies of the adiabatic extension of wires, carried out by Joule and Haga, have shown a good agreement with theory. It will be noted that along with experimental studies of the adiabatic compression of liquids, Joule and Haga's studies were among the first experimental tests of the second law of thermodynamics, the entropy principle.

For some bodies (rubber, some polymers) $\alpha < 0$, so that rods made from them contract upon heating. It follows then from formula (14.20) that $\left(\frac{\partial T}{\partial f}\right)_S > 0$, i.e. that a rod made from such material heats when acted on by a tensile force. This can easily be verified carrying out experiments with a rubber plait.

Problems

1. A copper rod having a length $l_0 = 1$ m is being stretched isothermally, with a tensile force of $f = 10^3$ N, $T = 300$ K. Young's modulus $E = 1.2 \times 10^{11}$ N/m^2, the linear extension coefficient $\alpha = 1.6 \times 10^{-5}$ deg^{-1}, the cross-sectional area $\sigma = 0.1$ cm^2. Find the work done on the rod, A, and the quantity of heat Q supplied from a thermostat (pay attention to the difference in the orders of magnitude of the quantities Q and A and explain the physical reason for this difference).

Answer. $A = \frac{l_0 f^2}{2E\sigma} \approx 0.4$ J, $Q = \alpha T f l_0 = 4.8$ J.

2. Plot on f-l and T-S planes the cycle consisting of the following three processes: (a) a rod is stretched isothermally at temperature T_1 with a tensile force f; (b) at $f = \text{const}$ the rod is cooled to temperature T_2; (c) the load is removed adiabatically and the rod reverts to its initial state. What is the form of this cycle when a rubber plait is used?

15. Thermodynamics of Magnetics

This section is devoted to the thermodynamic properties of para- and diamagnetic materials placed in an external magnetic field **H**. The thermodynamics of ferromagnetic materials is particularly complex, since phase transitions, that is the change of a ferromagnetic into a paramagnetic material are involved. The theory of ferromagnetic materials will be considered in Chapter VIII, devoted to the statistical theory of phase transitions (Sec. 78). As in the case of rods, we must have, firstly, the expression for elementary work and, secondly, the equation of state.

As is known from electrodynamics, the total elementary work done by the sources of a magnetic field to change the field and magnetize the substance upon a change in the induction vector by the quantity $d\mathbf{B}$, referred to one mole with volume V, is expressed by formula $\delta A = -\frac{V\mathbf{H}}{4\pi} d\mathbf{B}^*$. We shall limit ourselves to a consideration of uniform fields and homogeneous and isotropic magnetic materials. Here, the direction of vectors **H** and **B** coincides, and the formula for work acquires the form

$$\delta A = -\frac{VH}{4\pi} dB. \tag{15.1}$$

Just as with the thermodynamics of rods, the minus sign in (15.1) indicates that at $dB > 0$ the work is done by the external field on the magnetic material. It is clear from formula (15.1) that to pass over from the thermodynamics of gases to the thermodynamics of magnetic materials the following substitution must be made in the corresponding formulae:

$$P \to -\frac{VH}{4\pi}, \quad V \to B, \tag{15.2}$$

and the differential of the internal energy rewritten to read

$$dU = T\,dS + \frac{VH}{4\pi} dB. \tag{15.3}$$

* The Gaussian system of units is used in Secs. 15 and 16, devoted to electrical and magnetic phenomena.

The main thermodynamic indentity acquires in the Jacobian form the following form:

$$-4\pi\frac{\partial(T, S)}{\partial(HV, B)} = 1. \tag{15.4}$$

In this section the volume of one mole of a magnetic material, V, is assumed to be constant, i.e. we ignore the phenomena of magnetostriction and piezomagnetism that will be considered briefly in Sec. 20.

It is convenient to present the equation for work (15.1) in a somewhat different form. Making use of the relation $\mathbf{B} = \mathbf{H} + \frac{4\pi}{V}\mathbf{M}$, where $\mathbf{M}$ is the magnetization vector, or the mean magnetic moment per mole, expression (15.1) can be presented as the sum of two terms:

$$\delta A = \delta A' + \delta A'' = -d\left(\frac{VH^2}{8\pi}\right) - H\,dM. \tag{15.5}$$

Introducing a new thermodynamic function $U^* = U - \frac{VH^2}{8\pi}$, whose natural variables are S and M, we obtain for its differential

$$dU^* = T\,dS + H\,dM. \tag{15.6}$$

The calibration condition for absolute entropy in the Jacobian form will now be rewritten to read

$$\frac{\partial(T, S)}{\partial(H, M)} = -1, \tag{15.7}$$

and the standard substitution for passing from formulae for the thermodynamics of gases to formulae for the thermodynamics of magnetic materials will have the form

$$P \to -H, \qquad V \to M. \tag{15.8}$$

In doing so, one must realize clearly that U^* does not mean internal energy less the energy of a magnetic field in a vacuum. This follows from the fact that H represents the field intensity already changed by the presence of the magnetic material. In each concrete problem H can be found by solving equations of electrodynamics with boundary conditions ($B_{1n} = B_{2n}$, $H_{1t} = H_{2t}$), the result depending essentially on the shape and size of the magnetic material.

Let us now turn to an examination of the equation of state $f(B, H, T) = 0$ or $f(M, H, T) = 0$, considering in the first place *paramagnetic materials*, i.e. substances that can be magnetized only in the presence of an applied field and for which the direction of magnetization coincides with that of the applied field. We could construct the thermodynamics of paramagnetic materials using a purely phenomenological approach, not resorting to atomic and molecular models and taking from statistical physics only the form of the equa-

tion of state. We, however, prefer the qualitative treatment of the molecular model of paramagnetic materials to the purely phenomenological approach, since the former makes it possible to foresee the important properties of the equation of state (saturation, or maximum, magnetization), without using its explicit form.

From the molecular viewpoint a paramagnetic material is a substance every molecule of which has a magnetic moment. In the absence of an external magnetic field the magnetic moments of individual molecules are oriented at random and the sum of the magnetic moments is equal on the average to zero. After a magnetic field intensity H is applied, the prevailing orientation of the magnetic dipoles becomes parallel to the field, and magnetization M appears, differing from zero. With rising field intensity H and decreasing intensity, or rate, of thermal motion (with decreasing T) the degree of orientation of the elementary magnetic dipoles increases. The saturation (maximum magnetization) effect is observed: as $H \to \infty$ or $T \to 0$ the degree of orientation of the magnetic dipoles tends to unity, and $M \to M_0$. For each fixed value of the field intensity H and given temperature T there exists an intermediate value of magnetization, falling between $M = 0$ and $M = M_0$.

It is possible to draw an analogy between an ideal gas and a paramagnetic material. The internal energy U of ideal gases depends only on temperature and is independent of volume, i.e. $U = U(T)$.

Let us find the general form of the equation of state of gases for which $U = U(T)$. From formula $dS = \frac{\delta Q}{T}$ we obtain

$$dS = \frac{dU}{T} + \frac{P}{T} dV.$$

If $U = U(T)$, then $\frac{dU}{T}$ is a total differential, and the term $\frac{P}{T} dV$ is also a total differential, which is possible only if the volume V is a function of $\frac{P}{T}$. An ideal gas represents a special case of gases for which the equation of state has the form $V = f\left(\frac{P}{T}\right)$.

By analogy with ideal gases, let us assume that for paramagnetic materials the expression $U^* = U^*(T)$ is also valid (an ideal paramagnetic material). It follows from this that $M = f\left(\frac{H}{T}\right)$. Let us write down the equation of state of an ideal paramagnetic material in the dimensionless form, introducing as an argument $\frac{M_0 H}{RT}$:

$$\frac{M}{M_0} = L\left(\frac{M_0 H}{RT}\right). \tag{15.9}$$

The analytical form of the function $L(x)$ can be found only by the methods of statistical physics. We shall call it the *generalized*

Langevin function, or simply Langevin function; physical meaning of this function is the degree of orientation of the elementary magnetic moments. It will be seen below that there exist various functions $L(x)$, the classical Langevin function and a number of quantum Langevin functions. For this reason no use will be made of the $L(x)$ function in its explicit form, for to obtain most of the physical results only the following qualitative properties of all the $L(x)$ functions are important: at $x = \frac{M_0 H}{RT} \gg 1$ (strong fields and low temperatures) the saturation effect takes place and $L(x) \to 1$ as $x \to \infty$. On the contrary, at $x \ll 1$ (weak fields and high temperatures) the degree of orientation of the magnetic moments is small and $L(x) \ll 1$. At $x = 0$ the slope of the Langevin curve differs from zero: $L'(0) \neq 0$, and the expansion of the function $L(x)$ for small values of x begins with the term proportional to x:

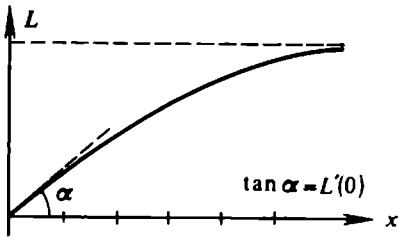


FIG. 27

$$L(x) \cong L'(0)\, x. \qquad (15.10)$$

Finally, both the Langevin function and its derivative $L'(x)$ are monotonic functions ($L(x)$ monotonically increases, and $L'(x)$ monotonically decreases), so that from the qualitative viewpoint the Langevin curve has the form depicted in Fig. 27.

With presently attainable magnetic fields $\frac{M_0 H}{RT} \ll 1$ nearly always holds (except for temperatures very close to zero) and

$$M = M_0 L\left(\frac{M_0 H}{RT}\right) \approx \frac{M_0^2 L'(0)}{RT} H = \chi_m H = \frac{A}{T} H. \qquad (15.11)$$

The quantity $\chi_m = \frac{M_0^2 L'(0)}{RT}$ is called the *magnetic susceptibility* of a substance, and formula (15.11) expresses the *Curie law*, according to which the magnetic susceptibility of a paramagnetic substance is inversely proportional to temperature.

Let us find now the form of the equation of state for diamagnetic substances. As is well known from electrodynamics, in the absence of a magnetic field the atoms of a diamagnetic substance do not have magnetic moments. After a magnetic field is applied a precession of electron shells arises around the direction of the magnetic field, the so-called *Larmor precession*. A more elementary description of this process is as follows; after a magnetic field is applied, currents are induced in the electron shells of an atom, and these currents do not attenuate when the field ceases to change, for there is no resistance

in the atomic contours. In accordance with the well-known Lenz law, the direction of these currents is such that the induced magnetic moments and, consequently, the magnetization are antiparallel to the external field. It is proved in electrodynamics that the magnetization of diamagnetic materials is proportional to the field intensity **H** (just as for paramagnetic materials far from saturation), but in contrast to paramagnetic substances, the susceptibility of diamagnetic materials is negative, $\chi_m < 0$.

Thus, the equation of state both for paramagnetic materials far from saturation and for diamagnetic materials can be presented in the general form:

$$\mathbf{M} = \chi_m (T)\, \mathbf{H}, \tag{15.12}$$

or

$$\mathbf{B} = \mu (T)\, \mathbf{H}, \tag{15.13}$$

where μ is the magnetic permeability, equal to

$$\mu (T) = 1 + \frac{4\pi\chi_m (T)}{V}. \tag{15.14}$$

The difference in the properties of various magnetic materials (in addition to the fact that for diamagnetic materials $\chi_m < 0$) manifests itself in the nature of the dependence of χ_m and μ on temperature. Classical Langevin paramagnetic materials were shown above (formula (15.11), $\chi_m = A/T$) to obey Curie's law and it was indicated that x_m is inversely proportional to temperature. At a constant density the susceptibility of rarified diamagnetic gases is independent of temperature, which is explained by the fact that thermal motion neither interferes with nor contributes to the appearance of induced magnetic moments. The nature of the dependence of χ_m and μ on temperature may be essentially different for crystalline magnetic materials: with rising temperatures atoms and molecules pass into excited states in which both the constant magnetic moments (paramagnetism) and the induced magnetic moments (diamagnetism) may become essentially different from the constant magnetic and induced magnetic moments in normal states. For this reason the dependence of the quantities χ_m and μ on temperature is specified by the concrete properties of a substance, and the functions $\chi_m' (T)$ and $\mu' (T)$ may be both positive and negative.

Let us now find the fundamental thermodynamic formulae for magnetic materials, first of all their entropy, limiting ourselves to the field-linear approximation $M = \chi_m (T) H$. Using formula (15.7), we obtain the expression for dS in variables T, M:

$$dS = \left(\frac{\partial S}{\partial T}\right)_M dT + \left(\frac{\partial S}{\partial M}\right)_T dM = \frac{C_M}{T} dT - \left(\frac{\partial H}{\partial T}\right)_M dM. \tag{15.15}$$

Taking into account the equation of state (15.12), we obtain

$$dS = \frac{C_M}{T}\,dT + \frac{\chi'_m M\,dM}{\chi_m^2}. \tag{15.16}$$

Since in a linear approximation $H \propto M$, then $\left(\frac{\partial C_M}{\partial M}\right)_T = 0$ [just as $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ for ideal and real gases and $\left(\frac{\partial C_l}{\partial l}\right)_T = 0$ for ideal rods], the first term in Eq. (15.16) and, consequently, the second term are total differentials. Based on Eq. (15.6) the differential of the function U^* is

$$dU^* = C_M\,dT + \frac{1+T\chi'_m/\chi_m}{\chi_m} M\,dM, \tag{15.17}$$

where both terms are also total differentials.

In particular, for Langevin ideal paramagnetic substances $\chi_m = A/T$, the expressions for entropy and internal energy are

$$S = \int \frac{C_M(T)\,dT}{T} - \frac{M^2}{2A} + \text{const}, \tag{15.18}$$

$$\tilde{U} = \int C_M(T)\,dT + \text{const}. \tag{15.19}$$

For perfect paramagnetic materials ($C_M = \text{const}$) we find that

$$S = C_M \ln T - \frac{M^2}{2A} + \text{const}, \tag{15.20}$$

$$\tilde{U} = C_M T + \text{const}. \tag{15.21}$$

For diamagnetic gases $\chi_m(T) = \text{const}$ and in accordance with formulae (15.16) and (15.17) we obtain at $C_M = \text{const}$

$$S = C_M \ln T + \text{const}, \tag{15.22}$$

$$\tilde{U} = C_M T + \frac{M^2}{2\chi_m} + \text{const}. \tag{15.23}$$

Just as in the case of rods and gases, we could compile an array of twelve thermodynamic coefficients and express them in terms of any three coefficients. In the case of magnetic materials it is convenient to select as two independent variables the quantities

$$\left(\frac{\partial M}{\partial T}\right)_H = \chi'_m(T)\,H, \quad \left(\frac{\partial M}{\partial H}\right)_T = \chi_m, \quad C_M(T).$$

Let us find the difference between the heat capacities, $C_H - C_M$. Making the standard substitution (15.8) in formula (11.23), we obtain

$$C_H - C_M = T\left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H^2. \tag{15.24}$$

Substituting $\left(\frac{\partial H}{\partial M}\right)_T = \chi_m^{-1}$ and $\left(\frac{\partial M}{\partial T}\right)_H = \chi'_m H$, we find

$$C_H - C_M = \frac{T(\chi'_m)^2}{\chi_m} H^2. \tag{15.25}$$

For diamagnetic gases the difference $C_H - C_M$ becomes zero and, using (15.11), we obtain for a Langevin paramagnetic material the expression

$$C_H - C_M = \frac{AH^2}{T^2} = L'(0) R \left(\frac{M_0 H}{RT}\right)^2, \tag{15.26}$$

and, consequently, at $\frac{M_0 H}{RT} \ll 1$ (far from saturation) the difference $C_H - C_M$ becomes rather small, just as the difference $C_f - C_l$ in the thermodynamics of rods.

Let us calculate the coefficient $\left(\frac{\partial T}{\partial H}\right)_S$, describing the temperature variation following an adiabatic demagnetizing (magnetizing) of a magnetic material. Making the standard substitution (15.8) in formula (11.24), we find

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H. \tag{15.27}$$

Let us define these formulae for a paramagnetic material, using formula (15.9). We have

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{M_0^2 H}{RTC_H} L'\left(\frac{M_0 H}{RT}\right).$$

If the paramagnetic material involved is far from saturation, $\left(\frac{M_0 H}{RT}\right) \ll 1$, then

$$\left(\frac{\partial T}{\partial H}\right)_S = L'(0)\left(\frac{M_0^2 H}{RC_H T}\right) = \frac{AH}{C_H T}.$$

As will be shown in Sec. 53, at low temperatures the heat capacity of solids is proportional to T^3, $C_H = \alpha T^3$, and

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{AH}{\alpha T^4}. \tag{15.28}$$

Since $\left(\frac{\partial T}{\partial H}\right)_S > 0$, an adiabatic disengagement of the field results in cooling. By virtue of the fact that $\left(\frac{\partial T}{\partial H}\right)_S \propto T^{-4}$, this method of obtaining low temperatures becomes very efficient when applied at an already low initial temperature. This explains why up until the present day the adiabatic demagnetizing method is the most effective technique of obtaining ultralow temperatures. It should, however, be noted that the substitution of $L'\left(\frac{M_0 H}{RT}\right)$ by $L'(0)$ becomes in-

valid at ultralow temperatures. Moreover, as $T \to 0$ the derivative $L'\left(\frac{M_0 H}{RT}\right)$ tends to zero and, consequently, the method of magnetic cooling, the same as any other cooling method, becomes ineffective, as follows from the Nernst heat theorem.

It is worth paying attention to one characteristic property of the M-H plane used in describing the phenomena associated with paramagnetic and diamagnetic materials. Let us place a non-magnetized magnetic material into a thermostat and apply the magnetic field H. Upon reaching the point at which magnetization is M, let us place the magnetic material into a thermally-insulated vessel and subject the substance to adiabatic demagnetizing Without considering how these processes are represented on the M-H plane (see the problem at the end of this section), it will be noted that at the end of the process of adiabatic demagnetizing we return to the origin of the coordinates ($H = 0$, $M = 0$)

The resulting "cycle", consisting of one isotherm and one adiabat, is that of a perpetual motion machine of the second kind (all the heat supplied along the isotherm is converted into work). In other words, contrary to what was said in Sec. 3, the adiabat and the isotherm intersect at two points. This paradox, an apparent violation of the second law of thermodynamics, is explained by the fact that the origin of the coordinates of the M-H plane does not describe unambiguously the state of a magnetic material. The non-magnetized magnetic material ($H = 0$, $M = 0$) may be at an arbitraty temperature and the process considered only appears to be a cyclic process. This is properly illustrated, for instance, on the M-T plane shown in Fig 29. The lack of one-to-one correspondence between the points on the M-T and M-H planes manifests itself formally in that the Jacobian used for passing over from the M-H plane to the M-T plane,

$$\frac{\partial (M, H)}{\partial (M, T)} = \left(\frac{\partial H}{\partial T}\right)_M = \frac{H}{T},$$

becomes zero at $H = 0$. It is clear that in the vicinity of the point $H = 0$, $M = 0$ the calibration $\frac{\partial (T, S)}{\partial (M, H)} = 1$ also becomes impossible since

$$\frac{\partial (T, S)}{\partial (M, H)} = \frac{\partial (T, S)}{\partial (T, M)} \frac{\partial (T, M)}{\partial (M, H)} = -\left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial T}{\partial H}\right)_M = -\frac{q_T}{H},$$

where q_T is the quantity of heat that must be supplied to the magnetic material when its magnetization is changed by unity, if the temperature of the substance is to remain constant; as $H \to 0$ this Jacobian increases infinitely.

Problems

1. Find the equation of the adiabat of a paramagnetic material plotted on the M-T and H-M planes in a linear approximation. Depict the "cycle" involving isothermal magnetizing and adiabatic demagnetizing on the H-M and M-T planes.

Solution. In a linear approximation we have

$$M = \frac{AH}{T}, \quad S(M, H) = C_M \ln\left(\frac{H}{M}\right) - \frac{M^2}{2A} + \text{const},$$

whence we find the equations of the adiabat and isotherm passing through the point H_0M_0 on the H-M plane:

$$H = \begin{cases} H_0 \dfrac{M}{M_0} \exp\left(\dfrac{M^2 - M_0^2}{2AC_M}\right) & \text{at } S = \text{const}, \\ \dfrac{T_0}{A} M & \text{at } T = T_0 = \text{const}. \end{cases}$$

The two curves are shown in Fig. 28.

The equation of the adiabat plotted on the T-M plane is $T = T_0 \exp \frac{M^2 - M_0^2}{2AC_M}$, and it can be seen in Fig. 29 that the magnetic material "returns" to the non-magnetized state at $M = 0$ with another temperature $T_1 = T_0 \exp\left(-\frac{M_0^2}{2AC_M}\right)$.

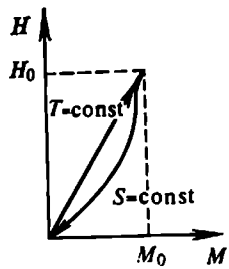


FIG. 28

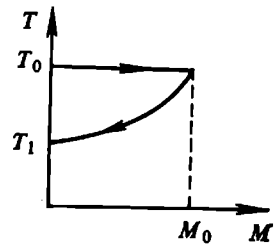


FIG. 29

2. Show that if $\frac{\partial C_M}{\partial M} = 0$, the dependence of χ_m on T must be expressed by $\chi_m = (BT + C)^{-1}$ (B and C are constants) and that this result is self-consistent.

Hint. Use the condition of the total differential for $dS(M, T)$ [formula (15.16)].

16. Thermodynamics of Dielectrics

Let us consider in this section the thermodynamic properties of polarizing media (dielectrics) placed in an external electric field **E**. As is well known from electrodynamics, the total elementary

work performed by the sources of an electric field upon a change in the induction vector by $d\mathbf{D}$, referred to one mole for a homogeneous and isotropic dielectric ($\mathbf{D} \parallel \mathbf{E}$), is expressed by the formula

$$\delta A = -\frac{V}{4\pi} E\, dD. \tag{16.1}$$

The work specified by formula (16.1) is the total work done by the sources of the field and spent both to change the field $\mathbf{E}$ created by these sources together with the bound charges of the dielectric, as well as to polarize the dielectric. It follows from formula (16.1) that to pass over from the thermodynamic formulae derived for gases to the thermodynamic formulae for dielectrics the following substitution must be made:

$$P \to -\frac{V}{4\pi} E, \quad V \to D, \tag{16.2}$$

and the differential of internal energy be presented in the form

$$dU = T\, dS + \frac{V}{4\pi} E\, dD. \tag{16.3}$$

The volume of the dielectric is assumed to be fixed, i.e. the electrostriction and the piezoelectric effect are ignored.

In the Jacobian form the basic thermodynamic identity is

$$-4\pi \frac{\partial (T, S)}{\partial (E, D)} = 1. \tag{16.4}$$

Let us represent the expression for work (16.1) in a somewhat different form —similar to the form (15.5) in the preceding section. Making use of the known relationship $\mathbf{D} = \mathbf{E} + \frac{4\pi}{V} \mathbf{p}$, where $\mathbf{p} =$ = polarization vector (average dipole moment per 1 kmole); $V =$ = volume of a kilomole, write down the work δA as the sum of two terms,

$$\delta A = \delta A' + \delta A'' = -d\left(\frac{VE^2}{8\pi}\right) - E\, dp. \tag{16.5}$$

Introducing the thermodynamic function $U^* = U - \frac{VE^2}{8\pi}$, whose natural variables are S and p, we obtain for the differential of this function the expression

$$dU^* = T\, dS + E\, dp, \tag{16.6}$$

and the calibration conditions for absolute entropy takes the form

$$\frac{\partial (T, S)}{\partial (E, p)} = -1. \tag{16.7}$$

The standard substitution for passing from the thermodynamic formulae for gases to those for dielectrics now has the form

$$P \to -E, \qquad V \to p. \tag{16.8}$$

As in the case of magnetic materials, here also it should be borne in mind that **E** represents a field intensity already changed by the presence of a dielectric substance, and that the intensity depends materially on the shape and size of the dielectric. This is why the function U^* does not have the direct physical meaning of internal energy less the energy of the electric field in a vacuum.

The equation of state for media that are polarized in an electric field, that is, for dielectrics, is the relation between the electric field intensity **E**, the polarization vector **p** and temperature. There are two different equations of state for dielectrics of two kinds—*nonpolar* and *polar*. In nonpolar dielectrics the molecules (atoms, crystal lattice cells) have no dipole moments in the absence of an external field. After a field **E** is applied, the positive and negative charges shift in opposite directions and the molecules acquire dipole moments, with the apparent polarization being, for not very strong fields, proportional to the applied field:

$$\mathbf{p} = \chi_e \mathbf{E}. \tag{16.9}$$

The quantity χ_e is called the *electric susceptibility* of matter, it is independent of temperature for nonpolar gaseous dielectrics. This follows qualitatively from the fact that thermal motion does not affect the deformation of the molecules of a dielectric acted upon by an electric field, just as it fails to influence the magnetizing of diamagnetic materials. Equation (16.9) is the equation of state of a nonpolar dielectric.

In polar dielectrics the elementary particles (atoms, molecules) have dipole moments even in the absence of an applied field. However, at $\mathbf{E} = 0$ these dipole moments are oriented at random and the polarization vector equals zero. In addition to the weak deformation of molecules, an applied electric field **E** causes a preferred orientation of the dipole moments parallel to the field and creates a polarization differing from zero. The theory of polarization of polar dielectrics is very similar to the magnetization theory devised for paramagnetic materials and leads to a result similar to that obtained in Sec. 15:

$$\frac{p}{p_0} = L\left(\frac{p_0 E}{RT}\right), \tag{16.10}$$

where p_0 = saturation polarization $\left(\text{reached at the limit } \frac{p_0 E}{RT} \gg 1\right)$;

L = Langevin function (having in this formula the meaning of the degree of orientation of elementary dipoles and

possessing the properties described in the preceding section).

In particular, in the case of weak fields and high temperatures $\left(\frac{p_0 E}{RT} \ll 1\right)$, most frequently encountered in practical applications, the Langevin function can be taken in a linear approximation $L(x) \approx L'(0)\, x$, and we actually obtain, similar to formula (15.11) in the preceding section, the expression (16.9), where

$$\chi_e = \frac{p_0^2}{RT} L'(0) = \frac{A}{T}.$$

Thus, there is a certain similarity in respect to the dependence of susceptibility on temperature between the thermodynamics of polar dielectrics and paramagnetic materials, on the one hand, and the thermodynamics of nonpolar dielectrics and diamagnetic materials, on the other. At the same time, electric and magnetic phenomena differ essentially in that the electric susceptibility χ_e is positive for any dielectric, while the magnetic susceptibility of diamagnetic materials is negative.

Thus, the equation of state both for polar dielectrics far from saturation and for nonpolar dielectrics can be presented in the form

$$\mathbf{p} = \chi_e(T)\,\mathbf{E}, \tag{16.11}$$

or

$$\mathbf{D} = \varepsilon(T)\,\mathbf{E}, \tag{16.12}$$

where $\varepsilon(T)$ is the *dielectric permeability* of a substance, equal to

$$\varepsilon(T) = 1 + \frac{4\pi}{V}\chi_e(T). \tag{16.13}$$

The thermodynamic formulae for dielectrics resemble the thermodynamic formulae derived for magnetic materials and they can be obtained from the relationships described in the preceding section by the substitution $H \to E$, $M \to p$ (the formal nature of this correspondence is clear from the fact that the vector **E** is the true averaged intensity of a microfield, whereas the vector **H** is some auxiliary quantity, and the true averaged intensity of the magnetic microfield is the magnetic induction **B**). This substitution permits us to obtain, for instance, from formula (15.15) the expression

$$dS = \frac{C_p}{T}\,dT - \left(\frac{\partial E}{\partial T}\right)_p dp. \tag{16.14}$$

Further, at p = const the intensity E is a linear function of temperature for polar dielectrics [this follows from formula (16.10)] or the intensity is constant for gaseous nonpolar dielectrics. It follows from this that just as for gases, rods and magnetic materials the heat capacity C_p depends only on temperature and the first term in Eq.

(16.14) is a total differential. In the second term the coefficient for polar dielectrics far from saturation is

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\chi_e' p}{\chi_e^2},$$

and for gaseous nonpolar dielectrics it equals zero.

By virtue of the foregoing, for polar dielectrics we have

$$dS = \frac{C_p}{T}\,dT + \frac{\chi_e'(T)}{\chi_e^2}\,p\,dp = \frac{C_p}{T}\,dT - \frac{p\,dp}{A}, \qquad (16.15)$$

and for nonpolar dielectrics

$$dS = \frac{C_p}{T}\,dT, \qquad (16.16)$$

whence, integrating, we find for polar dielectrics

$$S = C_p \ln T - \frac{p^2}{2A} + \text{const}, \qquad (16.17)$$

and for nonpolar dielectrics

$$S = C_p \ln T + \text{const}. \qquad (16.18)$$

In the case of polar dielectrics, from Eqs. (16.6) and (16.15) we have for the function U^*

$$dU^* = C_p\,dT, \quad U^* = C_p T + \text{const}. \qquad (16.19)$$

Taking into account that $\left(\frac{\partial P}{\partial T}\right)_E = 0$, we get for gaseous nonpolar dielectrics the following relationship:

$$dU^* = C_p\,dT + E\,dp = C_p\,dT + \frac{p\,dp}{\chi_e},$$

whence, at $\chi_e = \text{const}$, we find

$$U^* = C_p T + \frac{p^2}{2\chi_e} + \text{const}. \qquad (16.20)$$

As an exercise find the difference $C_E - C_p$ and the change in temperature for polar and nonpolar dielectrics undergoing adiabatic polarization. Some of these problems will be solved in Sec. 19 by another method. Finally, it should be noted, that the "paradox" considered at the end of the preceding section and associated with the invalidity of the p-E plane close to the point $p = 0$, $E = 0$ also appears when dealing with dielectrics.

Problems

1. Find the difference $C_E - C_p$ for polar and nonpolar dielectrics.

Answer. $C_E - C_p = T\frac{(\chi_e')^2}{\chi_e}E^2 = \begin{cases} 0 \text{ for nonpolar dielectrics,} \\ \frac{AE^2}{T^2} \text{ for polar dielectrics.} \end{cases}$

2. Find the change in temperature caused by an adiabatic application of the field E for polar and nonpolar dielectrics.

Answer. $\left(\frac{\partial T}{\partial E}\right)_S = -\frac{\chi_e' TE}{C_E}$;

$$\left(\frac{\partial T}{\partial E}\right)_S = \begin{cases} \frac{AE}{C_E T} \text{ for polar dielectrics,} \\ 0 \text{ for nonpolar dielectrics.} \end{cases}$$

17. Thermodynamics of Radiation

Let us consider an enclosure the walls of which are at a temperature T. Owing to the radiation from the walls the enclosure is filled with electromagnetic radiation characterized by all kinds of directions of propagation, polarization and frequencies. In equilibrium state an equal and time-independent *radiant energy density*, depending on temperature T, sets in at all points in the enclosure. Furthermore, the fact that the radiant energy density is the same at all points and the steady-state nature of the equilibrium state imply that an equal and constant spectral distribution of energy sets in which permits the introduction of the *spectral radiant energy density* $\rho(\nu, T)$, so that the product $\rho(\nu, T)\,d\nu$ is the quantity of radiant energy per unit volume for frequencies in the range between ν and $\nu + d\nu$. It is clear that the spectral density and the radiant energy density are related as follows:

$$u(T) = \int_0^\infty \rho(\nu, T)\,d\nu. \tag{17.1}$$

The internal energy of radiation is related to the radiant energy density as follows:

$$U = u(T)\,V. \tag{17.2}$$

It should be noted that a small hole in the wall of an enclosure represents with sufficient accuracy the model of a blackbody, since the radiation incident on this hole from the outside will partly be absorbed each time the radiation falls on the inside walls of the enclosure and be practically fully absorbed before leaving the en-

closure. In this connection equilibrium radiation in an enclosure is referred to as *blackbody radiation.*

It can readily be seen that the spectral density (and radiant energy density) of blackbody radiation is independent of the properties of the walls of the enclosure and is a universal function of frequency and temperature (but radiant energy density of temperature only).

In fact, let two such enclosures, whose walls are made from different materials but are at the same temperature, have, if only for one frequency ν, different spectral densities. Then, connecting the enclosures by a light guide with a filter that passes light only of frequency ν, we first obtain an energy flux from one enclosure to the other at equal temperatures, then from the enclosure at a lower temperature to the enclosure at a higher temperature, thus violating the laws of thermodynamics (see Sec. 10).

Let us introduce along with function $\rho(\nu, T)$ the spectral emissive power of a blackbody. The quantity $\varepsilon(\nu, T)$ determines the amount of energy emitted from a unit surface area of a blackbody per unit time. It will be shown that the quantity $\varepsilon(\nu, T)$ differs from the function $\rho(\nu, T)$ only by the factor of $c/4$. Owing to the isotropic nature of blackbody radiation, each point of the enclosure emits a flux of energy that is uniformly distributed in all directions (per unit of solid angle) and is equal to $\frac{c}{4\pi}\rho(\nu, T)$. The energy flux incident on unit area of the enclosure per unit time at an angle θ to the normal in the solid angle $d\Omega = 2\pi \sin\theta\, d\theta$ is equal to $\frac{c}{4\pi}\rho(\nu, T)\cos\theta\, d\Omega = \frac{c}{2}\rho(\nu, T)\sin\theta\cos\theta\, d\theta$. The same quantity of energy is emitted in the equilibrium state. Integrating this expression over a hemisphere, we obtain the spectral emissivity (emittance)

$$\varepsilon(\nu, T) = \frac{c}{2}\rho(\nu, T)\int_0^{\pi/2}\sin\theta\cos\theta\, d\theta = \frac{c}{4}\rho(\nu, T). \qquad (17.3)$$

Integrating Eq. (17.3) over frequencies, we obtain the expression for the total emissivity of a blackbody $E(T)$:

$$E(T) = \int_0^{\infty}\varepsilon(\nu, T)\, d\nu = \frac{c}{4}u(T). \qquad (17.4)$$

If radiation is considered as a photon gas, then the fact that energy density $u(T)$ depends only on temperature, not on volume, causes the photon gas to resemble a saturated vapour. In fact, when a vapour is being compressed by a piston, a fraction of its molecules passes into the liquid phase, and at a constant temperature the energy density (or the energy per molecule) remains constant. By

analogy, when a photon gas is compressed with the aid of a piston, a fraction of the photons can be expected to be absorbed by the walls of the enclosure and of the piston, and so the energy density remains constant. It may therefore be assumed that a photon gas, like a saturated vapour, is not an elastic substance, i.e. that similar to the pressure of a saturated vapour, the pressure of a photon gas is independent of volume and depends only on temperature.

The foregoing reasoning cannot, of course, be taken as proof and it does not fit the framework of thermodynamics; however, this reasoning elucidates the form taken by the equation of state for the radiation phenomenon.

This equation will be proved in Sec. 52, taking radiation as a photon gas. It can also be obtained from Maxwell's classical equations of electrodynamics, and represents the pressure of isotropically incident radiation of light, i.e. incident at all possible angles upon any surface, as equal to one third of the radiant energy density and, consequently, dependent only on temperature:

$$P = \frac{1}{3} u\,(T) \tag{17.5}$$

Equations (17.2) and (17.5), combined with the expression (11.25) for the derivative $\left(\frac{\partial U}{\partial V}\right)_T$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T}\right] \tag{17.6}$$

make it possible to find the dependence of u on temperature. Substituting Eqs. (17.2), (17.5) into Eq. (17.6), we obtain

$$4u\,(T) = Tu'(T).$$

Upon integration of the above formula we obtain for the radiant energy density the following expression:

$$u\,(T) = \sigma T^4, \tag{17.7}$$

and for the total emissivity $E\,(T)$ the expression

$$E\,(T) = \frac{c\sigma}{4} T^4 = aT^4. \tag{17.8}$$

Formula (17.8) expresses the well-known *Stefan-Boltzmann law* for the radiant energy density. The numerical values of the quantities a and σ cannot be found by thermodynamic methods. The numerical value of a (it can be computed by the methods of statistical physics as shown in Sec. 52) equals

$$a = 5.67 \times 10^{-8}\ \text{J/m}^2 \cdot \text{s} \cdot \text{deg}^4.$$

Let us calculate the entropy of equilibrium radiation, assuming that

$$dS = \frac{dU + P\,dV}{T} = \frac{d(uV) + \frac{u}{3}\,dV}{T} = \frac{4}{3}\sigma T^3\,dV + 4\sigma V T^2\,dT.$$

Integrating the total differential, we find

$$S = \frac{4}{3}\sigma T^3 V + \text{const}. \tag{17.9}$$

Thus, the equation of the adiabat representing equilibrium radiation has the following form:

$$T^3 V = \text{const}.$$

Making use of formula (17.9), we can find the heat capacity

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = 4\sigma T^3 V. \tag{17.10}$$

The heat capacity at constant pressure is evidently meaningless [since $P = P(T)$] and, formally, $C_P = \left(\frac{\delta Q}{\delta T}\right)_P = \pm\infty$.

As to the spectral radiant energy density $\rho(\nu, T)$, it cannot be determined by thermodynamic methods and requires the application of statistical physics. Thermodynamics, however, also makes it possible to obtain some important information on the form of the function $\rho(\nu, T)$. These data constitute the essence of Wien's law, to be derived below.

To derive Wien's law, it is sufficient to use the reasoning associated with dimensions, and the Stefan-Boltzmann law.

From the viewpoint of classical physics the formula specifying the spectral radiant energy density, $\rho(\nu, T)$, can include the quantities ν, T and two universal constants: the velocity of light in a vacuum c and the gas constant R. It is convenient, however, to replace the gas constant by the *Boltzmann constant* $k = \frac{R}{N_A}$, since the two constants are interrelated. Assuming as basic quantities energy (dimension ε), length (dimension λ), time (dimension τ) and temperature (dimension θ), the quantities $\rho(\nu, T)$, ν, T, c, k have the dimensions

$$[\rho] = \varepsilon\tau\lambda^{-3}, \quad [\nu] = \tau^{-1}, \quad [T] = \theta, \quad [c] = \lambda\tau^{-1}, \quad [k] = \varepsilon\theta^{-1}.$$

Let us assume that $\rho(\nu, T)$, accurate to some dimensionless factor Λ, is a product of ν, T, c, k raised to some powers:

$$\rho'(\nu, T) = \Lambda\nu^m T^n c^p k^q.$$

Equating the dimensions of the basic quantities on the left- and right-hand sides of the last equality, we obtain $m = 2$, $n = 1$,

$p = -3$, $q = 1$ and, consequently, the unknown dependence has the form

$$\rho(\nu, T) = \Lambda \frac{kT}{c^3} \nu^2. \tag{17.11}$$

It will be shown in Sec. 52 that classical statistical physics leads to exactly the same result, with the remaining undetermined factor Λ being equal to 8π. The law expressed by formula (17.11) is referred to as the *Rayleigh-Jeans law* and agrees well with experimental data at small radiation frequencies; at high radiation frequencies, however, there is a great variance between the data calculated by the formula for the Rayleigh-Jeans law and experimental results, indicating that, being a function of frequency, $\rho(\nu, T)$ has a maximum at a certain frequency, then diminishes with rising frequency. The Rayleigh-Jeans law, asserting that the quantity $\rho(\nu, T)$ increases indefinitely with frequency ν, leads to the absurd conclusion that the equilibrium radiant energy density $u(T)$ [see Eq. (17.1)] is infinitely large—a paradox, known in the history of physics as the *ultraviolet catastrophe.*

In order to avoid this paradox and obtain an intelligent result, we have to leave the framework of classical physics and assume the existence of one more universal constant, h, not appearing in statements of the classical laws, and allow for its presence in the definition of $\rho(\nu, T)$. This means that the dimensionless factor Λ is not constant quantity and actually depends on some combination of the new constant and the quantities ν and T, assuming that the frequency ν present in this combination is not raised to any power (otherwise we would have raised the argument of the function to an appropriate power to make the exponent in ν equal to unity), and temperature T is raised to some power r.

Denoting the coefficient at ν by $\frac{h}{k}$, we obtain

$$\Lambda = \Lambda\left(\frac{h\nu T^r}{k}\right), \quad \rho(\nu, T) = \Lambda\left(\frac{h\nu T^r}{k}\right)\frac{kT}{c^3}\nu^2.$$

Let us determine now the exponent r, imposing the requirement that the Stefan-Boltzmann law be valid for $u(T)$. Formula (17.1) yields

$$u(T) = \frac{kT}{c^3}\int_0^\infty \nu^2 \Lambda\left(\frac{h\nu T^r}{k}\right) d\nu$$

or, introducing the integration variable $y = h\nu T^r/k$

$$u(T) = \frac{8k^4 T^{1-3r}}{c^3 h^3}\int_0^\infty y^2 \Lambda(y)\, dy.$$

Since the entire dependence on temperature is now determined by the factor T^{1-3r} to ensure the agreement with the Stefan-Boltzmann law it is required that $1 - 3r = 4$, i.e. $r = -1$.

Thus, we obtained for $\rho(\nu, T)$ the expression

$$\rho(\nu, T) = \frac{kT}{c^3}\nu^2\Lambda\left(\frac{h\nu}{kT}\right). \tag{17.12}$$

Formula (17.12) is the mathematical statement of *Wien's law.*

It can be readily seen that the dimension of the new constant h equals the dimension of action $[h] = \varepsilon\tau$. It should be noted that, as will be shown below, in statistical physics the constant k coincides with Planck's constant, and its appearance in the physical laws governing radiation is associated with the important part played by quantum regularities in radiation phenomena.

Multiplying the numerator and the denominator in (17.12) by ν, we present Wien's law in the more commonly encountered form:

$$\rho(\nu, T) = \nu^3 f\left(\frac{\nu}{T}\right). \tag{17.13}$$

Thus, Wien's law reduces the problem of finding the function of two variables $\rho(\nu, T)$ to that of determining the function of one variable, $f\left(\frac{\nu}{T}\right)$ $\left[\text{or } \Lambda\left(\frac{h\nu}{kT}\right)\right]$.

The Wien law allows us to formulate an important rule determining the location of the maximum emitted energy in the spectrum of blackbody radiation. Differentiating (17.12) with respect to ν and equating the derivative to zero, we obtain

$$\frac{\partial\rho(\nu, T)}{\partial\nu} = \frac{kT\nu}{c^3}\left[2\Lambda\left(\frac{h\nu}{kT}\right) + \frac{h\nu}{kT}\Lambda'\left(\frac{h\nu}{kT}\right)\right] = 0 \tag{17.14}$$

at $\nu = \nu_m$.

Denoting $\frac{h\nu_m}{kT} = z$, we obtain the equation

$$2\Lambda(z) + z\Lambda'(z) = 0. \tag{17.15}$$

Experimental studies have shown the curve representing the frequency dependence of ρ at a fixed temperature to have but one maximum and, consequently, Eq. (17.15) has only one positive root $z = b$, i.e.

$$\frac{h\nu_m}{kT} = b. \tag{17.16}$$

Thus we have obtained Wien's displacement law, indicating that as the temperature of an emitting body increases, the energy maximum shifts to the high-frequency range of the spectrum, and vice versa.

Substituting formula (17.16) into formula (17.13), we obtain the

maximum value of $\rho(\nu, T)$:

$$\rho(\nu_m, T) = AT^3, \tag{17.17}$$

where $A = \frac{k^3 b^3}{c^3 h^3} \Lambda(b)$ is constant. The value of $\rho(\nu_m, T)$ is proportional to the cubed absolute temperature.

It should be emphasized once more that the derivation of Wien's law is all that can be obtained by applying the thermodynamic method to the theory of radiation. The exact form of the function $\Lambda\left(\frac{h\nu}{kT}\right)$ and, consequently, the numerical value of the constant b in Wien's displacement law and the constant a in the Stefan-Boltzmann law cannot be found by thermodynamic methods, and the problem has to be solved by applying the statistical method.

Problems

1. A spherical blackbody having radius $R = 0.1$ m and initial temperature $T_1 = 1000$ K is cooled by radiation. The surrounding medium is at a temperature $T = 0$ K. What time will it take for the temperature of the sphere to drop to $T_2 = 100$ K? The heat capacity $C = 5 \times 10^2$ J/kg·deg, the density $\rho = 8 \times 10^3$ kg/m^3.

Answer. $t = \frac{\rho CR}{9\sigma}(T_2^{-3} - T_1^{-3}) = 220$ hours.

2. Find the isothermal K_T and the adiabatic K_S compressibility of blackbody radiation.

Answer. $K_T = \pm\infty$, $K_S = \frac{9}{4aT^4}$.

18. Thermodynamics of Water

It was shown in Secs. 15 and 16 that the calibration of absolute temperature and absolute entropy, expressed by Eqs. (15.7) and (16.7), becomes invalid close to the origin of the coordinates on the M-H plane (and, correspondingly, on the p-E plane), due to the lack of one-to-one correspondence between the points on these planes and the physical states of a system (the state $M = 0$, $H = 0$ or $E = 0$, $p = 0$ can occur at any temperature).

Let us now consider by way of example a thermodynamic system for which the calibration of absolute temperature and absolute entropy $\frac{\partial(T, S)}{\partial(P, V)} = 1$ [see (4.1)] cannot be employed in the vicinity of a certain line. It then becomes rather inconvenient to use the P-V and T-S planes to describe thermodynamic properties, such an approach obviously being inadequate for the physical essence of the problem.

It should, however, be emphasized that the exceptions are rather rare (for instance, water and some liquids, and also some solids), with the invalidity of the calibration (4.1) covering only small part of the P-V plane. But this calibration is suitable for most thermodynamic systems and for a large part of the T-S plane and the (generalized force)-(generalized coordinate) plane, and it is in order to use the Jacobian method to solve practical problems.

Most of the thermodynamic formulae derived in Secs. 1 through 11 are true not only for gases but also for liquids. However, when dealing with liquids it is considerably more difficult to obtain concrete results from the common thermodynamic formulae, inasmuch as no universal equation of state exists that would be suitable for all liquids, in contrast to ideal gases which all obey the equation of state $RT = PV$, and real gases the properties of which are approximately described by the van der Waals equation. Some of the common properties of liquids can be identified only qualitatively (for instance, the fact that their compressibility is very low compared to gases), while the other properties of liquids are of a somewhat individual nature, usually described by empirical relationships that are different for different liquids.

We shall limit ourselves to a qualitative study of the thermodynamic properties of water and some other liquids, for instance, silver iodide, the characteristic feature of which is the so-called *thermal anomaly*, i.e. the fact that the isobaric thermal expansion coefficient changes its sign at a certain temperature T_0. So, for water the derivative $\left(\frac{\partial V}{\partial T}\right)_P$ is positive at $t > 4$ °C, negative at $t < 4$ °C and equal to zero at $t = 4$ °C.

For substances characterized by such anomalous behaviour the calibration (4.1) cannot be applied at the anomaly points. In fact, the physical principle that is valid for any homogeneous physical system is the basic thermodynamic identity

$$dU = T\,dS - P\,dV.$$

The total differential requirement gives

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{18.1}$$

or

$$\frac{\partial (T, S)}{\partial (V, S)} = \frac{\partial (P, V)}{\partial (V, S)}. \tag{18.2}$$

However, to obtain the calibration (4.1), we have to divide the last equation by the Jacobian

$$\frac{\partial (P, V)}{\partial (P, S)} = \frac{\partial (P, V)}{\partial (P, T)} \frac{\partial (P, T)}{\partial (V, T)} \frac{\partial (V, T)}{\partial (V, S)} = \frac{T}{C_V} \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P,$$

becoming zero at the anomaly points; because of this the calibration is not used in this section.

Let us consider the thermodynamic properties of water on the T-V plane. It should be noted that the Jacobian of transformation from the P-V plane to the T-V plane is

$$\frac{\partial (P, V)}{\partial (T, V)} = \frac{\partial (P, V)}{\partial (P, T)} \frac{\partial (P, T)}{\partial (T, V)} = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad (18.3)$$

and becomes zero at the anomaly line L (Fig. 30). This makes the study of the thermodynamic properties of water very instructive, since in this situation the theorem of one-to-one correspondence between points in the small regions of the T-V and P-V planes becomes invalid.

Let us find qualitatively the shape of the isobars and adiabats on the T-V plane. The slope of the adiabat on this plane is

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P};$$

it is positive above the line L, negative below it and $\pm\infty$ on it (Fig. 30). It follows that the isobars having a vertical tangent intersect the line L, and the line L itself is the locus of the points at which the volume is at its minimum for $P = \text{const}$.

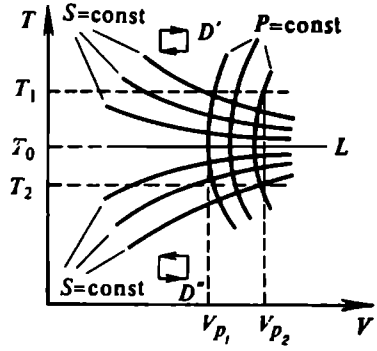


FIG. 30

Let us now consider the adiabats plotted on the T-V plane. According to Eq. (18.1), the slope of an adiabat is expressed by

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial (P, V)}{\partial (V, S)} = \frac{\partial (P, V)}{\partial (P, T)} \frac{\partial (P, T)}{\partial (V, T)} \frac{\partial (V, T)}{\partial (V, S)}$$

$$= \frac{T}{C_V} \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \qquad (18.4)$$

Since $\left(\frac{\partial P}{\partial V}\right)_T < 0$, the slope of the adiabats in respect to the V-axis is negative above the line L and positive below the line. Let us make sure that the line L is an isotherm. Assume that along some section of the line L its slope is, for instance, negative on the T-V plane. Then, according to Eq. (18.4), there exists in the region below the line L an adiabat (Fig. 31) that intersects the line L at a certain point (this adiabat has a positive slope). The adiabat has a horizontal tangent at the point of intersection, and its slope becomes negative in the region above the line L. Thus, on the T-V plane

the adiabat $S = \text{const}$ would then have a maximum and would intersect some isotherms at two points, which contradicts the entropy principle. By analogy, if the line L had a positive slope along a certain section, then some of the adiabats would have minimum points near the line L and would also intersect the isotherms twice. Thus, the line L must be an isotherm and, as follows from (18.4), the line is simultaneously a limiting adiabat whose slope $\left(\frac{\partial T}{\partial V}\right)_S = 0$. The appearance of the adiabats and isobars plotted on the T-V plane is shown in Fig. 30.

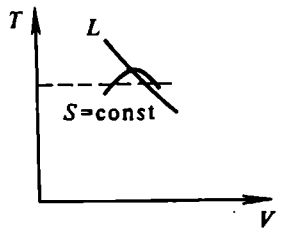


FIG. 31

It is interesting to note that the requirement that the line L be an isotherm leads to the equality $\left(\frac{\partial V}{\partial T}\right)_P = f(T)$, upon integration of which we obtain a somewhat unexpected form for the equation of state $V = f_1(T) + f_2(P)$; in this form, however, the equation of state can be valid only in close vicinity to the line L (close to temperature T_0). This result is in good agreement with the often applied empirical equation of state for liquids, $V = V_0 [1 + \alpha (T - 273) - K_T P]$.

Let us consider now the seeming paradox indicated by Sommerfeld [1]. Multiplying the two sides of Eq. (18.2) by the Jacobian $\frac{\partial (V, S)}{\partial (T, P)}$, we obtain

$$\frac{1}{T}\left(\frac{\delta Q}{\delta P}\right)_T = \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{18.5}$$

where $\left(\frac{\delta Q}{\delta P}\right)_T$ is the quantity of heat that must be supplied or removed upon a change in pressure by unity in order for the temperature to remain constant. Consider a Carnot cycle with water as the working medium, with the temperature of the heater above 4 °C and the temperature of the cooler below 4 °C. Then, along the section of isothermal expansion the pressure drops, $\delta P < 0$, and, on the other hand, $\left(\frac{\partial V}{\partial T}\right)_P > 0$. It follows that according to Eq. (18.5) $\delta Q > 0$—heat is supplied to the working medium. The pressure increases along the section of isothermal compression, $\delta P > 0$, but $\left(\frac{\partial V}{\partial T}\right)_P > 0$. It follows that $\delta Q > 0$ along this section as well. Since the other processes making up the Carnot cycle proceed adiabatically, we obtain a machine that converts all the supplied heat into work, i.e. a perpetual motion machine of the second kind, which violates the laws of thermodynam-

ics. The "paradox" is readily explained by considering Fig. 31, which shows that there are no adiabats connecting the isotherms arranged above and below the isotherm L and, consequently, it is impossible to realize a Carnot cycle in which the temperature of the heater $T_1 > T_0$ and the temperature of the cooler $T_2 < T_0$.

Let us now consider the thermodynamic behaviour of water, plotting the processes on the P-V plane.

On the P-V plane the isotherm-adiabat L is represented by the curve L' steeply falling due to the low compressibility of water. The curve L' divides the P-V plane into two regions, region I and region II (Fig. 32). It is easily seen that region I is not a physical region since no real states of water exist that would correspond to the points lying in that region. It follows from the fact that, as shown in Fig. 30, for each fixed pressure P there exists a minimum volume V_P, corresponding to the point of intersection of the isobar P = const with the isotherm L.

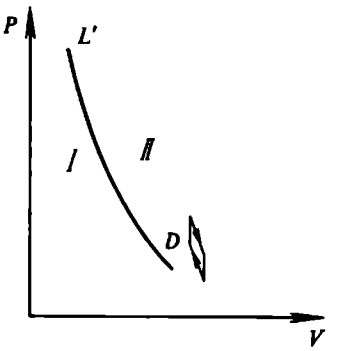


FIG. 32

Conversely, each point in region II represents two different physical states. In fact, Fig. 30 shows that each isochor intersects the isobar at two points, having different ordinates T_1 and T_2 and, consequently, two different points on the T-V plane merge into one point on the P-V plane, located in region II.

Let us point out one more curious property of the ambiguous correspondence. If we consider not a point, but a small cyclic process on the P-V plane in the doubly degenerate region II, then there exist on the T-V plane two different cyclic processes corresponding to it, one above and one below the line L. The two cycles depicted on the T-V plane will be seen to be oppositely directed.

Consider in region II of the P-V plane the small cyclic process D (Fig. 32) made up of two isotherms and two isochors circumvented in the clockwise direction ($\delta A > 0$). Corresponding to this cycle on the T-V plane are two cycles D' and D'', as shown in Fig. 30. The areas of the two cycles are specified by the formula

$$\delta T\, \delta V = \delta P \left(\frac{\partial T}{\partial P}\right)_V \delta V = \delta A \left(\frac{\partial T}{\partial P}\right)_V.$$

We made use of the fact that it is possible to substitute approximately on each isochor $\delta P \left(\frac{\partial T}{\partial P}\right)_V$ for δT. But for the cycle D' lying above

the line L the quantity $\left(\frac{\partial T}{\partial P}\right)_V$ is positive, and since $\delta A > 0$, the area of this cycle is also positive. Consequently, the cycle D' is circumvented clockwise. Cycle D'' lies below the line L, and so is circumvented counterclockwise.

So, a cyclic process created to perform as a heat engine and ensuring a gain in work, $A > 0$, is depicted on the T-V plane by a closed curve, with the cycle proceeding clockwise if located above the line L, and counterclockwise when below it. For a cyclic process required to perform as a cooler ($A < 0$), the cycle is circumvented in the opposite direction.

The Carnot cycle, for which T_0 is the isotherm of the heater and the cooler, degenarates into a section of the isotherm-adiabat L.

So, the P-V plane is of little use in representing graphically the thermodynamic properties of water, due to the fact that there exists no one-to-one correspondence between the physical properties of water and the points on the plane. The situation is even worse with the T-S plane, on which the isotherm-adiabat L simply cannot be presented as a two-dimensional continuum, since it degenerates into a point. This is why the T-V plane is the most useful for adequately reflecting the physics of the phenomena. It will be noted, however, that states of water at a distance far from the anomaly point can be successfully considered on the P-V and T-S planes and the calibration $\frac{\partial (T, S)}{\partial (P, V)} = 1$ can be used for such states.

Problem

Investigate the validity of the T-P and S-P planes in the neighbourhood of the isotherm-adiabat L to describe the thermodynamic behaviour of water. Represent qualitatively the adiabat and isochor on the T-P plane and the isotherm and isochor on the S-P plane.

19. The Thermodynamic Potential. Method of Thermodynamic Functions

In Secs. 6 and 13 we have introduced three thermodynamic potentials.

The *internal energy* (adiabatic potential), for which S and V are the natural variables,

$$U = U(S, V), \quad dU = T\,dS - P\,dV,$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S. \tag{19.1}$$

The *free energy* (isothermal potential), for which T and V are the natural variables,

$$F(T, V) = U - TS, \quad dF = -S\,dT - P\,dV,$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{19.2}$$

The *heat content* (enthalpy), for which the natural variables are S and P,

$$W(S, P) = U + PV, \quad dW = T\,dS + V\,dP,$$
$$T = \left(\frac{\partial W}{\partial S}\right)_P, \quad V = \left(\frac{\partial W}{\partial P}\right)_S. \tag{19.3}$$

The transformations $F = U - TS$ and $W = U + PV$ are referred to as the *tangential transformations* or the *Legendre transformations* (in the variables T, S and P, V respectively) and they offer a general method of obtaining new thermodynamic functions.

There exists one more pair of variables T, P that can be composed of the two pairs T, S and P, V, taking one variable from each pair. To obtain a characteristic thermodynamic function for these variables, let us apply the Legendre transformation to U for the two pairs of variables T, S and P, V, i.e. add to the two sides of Eq. (19.1) the quantity $d(PV - TS)$. The result is the *Gibbs thermodynamic potential* (or simply thermodynamic potential) for which the natural variables are T and P:

$$\Phi = U - TS + PV = F + PV = W - TS,$$
$$d\Phi = -S\,dT + V\,dP,$$
$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_P, \quad V = \left(\frac{\partial \Phi}{\partial P}\right)_T. \tag{19.4}$$

Knowing any of the thermodynamic functions expressed in terms of their variables, we are able in principle to find all the thermodynamic parameters of a system, including its heat capacity, and the equation of state.

For instance, knowing $\Phi(T, P)$, formula $S = -\left(\frac{\partial \Phi}{\partial T}\right)_P$ is used to find the entropy and, consequently, the heat capacity $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ and formula $\left(\frac{\partial \Phi}{\partial P}\right)_T = V$ is used to relate P, V, T, i.e. to find the equation of state.

It should, however, be emphasized that, on the other hand, thermodynamics provides only the relations between thermodynamic functions and their derivatives, permitting the solution of a number of concrete thermodynamic problems when one thermodynamic function is known. But to find any of the thermodynamic functions in

explicit form, we must know the equation of state and the dependence of the heat capacity on temperature. (It should be recalled that the derivatives of the type $\left(\frac{\partial C_V}{\partial V_T}\right)$, $\left(\frac{\partial C_l}{\partial l}\right)_T$, etc. can be found by the thermodynamic method.) In fact, even to determine the internal energy U we must know the derivatives

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V.$$

Thus, the relation between the information contained in the thermodynamic potentials (U, F, W, Φ), on the one hand, and the information contained in the equation of state and in the dependence of heat capacity on temperature, on the other hand, is of a dual nature.

Knowing the thermodynamic functions expressed in terms of their own variables, the thermodynamic relations can be used to obtain complete information on a system and, in particular, to find the equation of state and the heat capacity, and also the compressibility, the coefficient of thermal expansion and any thermodynamic coefficients. It will be shown below that it is precisely this approach that is followed in statistical physics: first, the thermodynamic functions are calculated independently with the aid of the formulae of statistical physics, then the thermodynamic relations (19.1) through (19.4) are used to find the equation of state and the heat capacity.

On the other hand, to find the thermodynamic functions within the framework of thermodynamics we must know the equation of state and the dependence of the heat capacity on temperature. The form of these relationships must be taken from statistical physics or determined experimentally.

It should be noted that many of the relations between thermodynamic coefficients, derived in Sec. 11 by application of Jacobians, can be obtained in a simpler way, making use of the fact that the expressions for dU, dF, dW, $d\Phi$ are total differentials. So, formula (11.11) is the condition for $d\Phi$ (T, P) to be a total differential, and formula (11.10) is a similar condition for dF (T, V).

It should be noted, however, that an equation of state, entropy and heat capacity can be found by simple differentiation only when the thermodynamic potentials are given as functions of their arguments. But if a thermodynamic potential is given in variables other than its natural variables, the problem reduces to a partial differential equation whose solution requires that some boundary condition be given.

One should note that cases when a thermodynamic function is given in variables other than its own can be divided into two types (we shall restrict ourselves to a discussion of cases when only one of the two arguments of a thermodynamic function is a "foreign" one).

Case 1. The argument T is replaced by S or vice versa. The boundary condition required is then provided by the Nernst heat theorem, according to which at $T = 0$ the entropy equals zero.

Let, for instance, the internal energy be given as a function of T and V instead of S and V. Since the variables T, V are the natural variables of free energy, let us pass over to the potential given in these variables, making use of the relation between U and F:

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V. \tag{19.5}$$

This equation is called the *Gibbs-Helmholtz fundamental equation.* To integrate Eq. (19.5), divide both its sides by T^2 and present the equation obtained in the following form:

$$\frac{T(\partial F/\partial T)_V - F}{T^2} = \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -\frac{U}{T^2}, \tag{19.6}$$

whence we have

$$F = -T\int_0^T \frac{U(T', V)}{(T')^2}\,dT' + \varphi(V)\,T, \tag{19.7}$$

where $\varphi(V)$ is an arbitrary function of volume that can be found by calculating the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \int_0^T \frac{U(T', V)}{(T')^2}\,dT' + \frac{U(T, V)}{T} - \varphi(V)$$

$$= \psi(T, V) - \varphi(V), \tag{19.8}$$

whence, in accordance with the Nernst heat theorem, we find $\varphi(V) = \psi(0, V)$, obtaining, thereby, the free energy as a function of its natural variables T and V.

The cases when the free energy is given as a function of S and V, the heat content as a function of T and P and Gibbs' potential as a function of S and P can be considered in a similar way. The Nernst heat theorem allows us to define in all these cases one of the thermodynamic potentials in its own variables, and, consequently, to obtain comprehensive thermodynamic information on the system involved. It should, however, be noted that the procedure described above, of passing to the natural potential, cannot always be realized. When the initial potential, given in foreign variables, is known for a certain range of parameters and the extrapolation to $T \to 0$ is impossible, it becomes impossible to apply the Nernst heat theorem.

A simple example is that of an ideal gas for which U is expressed in terms of T, V by formula $U = C_V T$ and the integral in (19.7) and (19.8) happens to be a divergent integral (for an ideal gas, as $T \to 0$, C_V tends to the constant $\frac{3}{2}R$, see Sec. 40). This indicates

that the concept of an ideal gas is invalid at very low temperatures. The same follows from formula (4.5) of the entropy of an ideal gas, that formally leads to $S \to -\infty$ at $T \to 0$, which is in contradiction to the Nernst heat theorem. Naturally, all the foregoing reasoning does not mean that it is impossible to find the free energy of an ideal gas, but it does show that the information contained in the formula $U = C_V T$ is insufficient for this purpose (free energy can be found by formula $F = U - TS$, inasmuch as the entropy is already known).

Case II. The argument P is replaced by V or vice versa. For instance, let the free energy be known as a function of T and P, instead of T and V. It will be seen below that such information is of virtually no use in finding the thermodynamic properties of a system. Passing to Gibbs' potential in its natural variables T and P, we have

$$F(T, P) = \Phi - PV = \Phi - P\left(\frac{\partial \Phi}{\partial P}\right)_T \tag{19.9}$$

Dividing both sides of Eq. (19.9) by P^2 and integrating, we obtain

$$\Phi = -P\int_0^P \frac{F(T, P')\,dP'}{(P')^2} + P\varphi(T),$$

whence we find

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_P = P\int_0^P \frac{F(T, P')\,dP'}{(P')^2} - P\varphi'(T).$$

This should convince us that the Nernst heat theorem allows us only to find $\varphi'(0)$, which clearly adds nothing to what we already know about the system involved. This is why we can determine by formula (19.9) only the dependence of Φ on pressure. In particular, differentiating both sides with respect to P, we find

$$V = \left(\frac{\partial \Phi}{\partial P}\right)_T = -\int_0^P \frac{F(T, P')\,dP'}{(P')^2} - \frac{F(T, P)}{P} + \varphi(T), \tag{19.10}$$

and only the compressibility

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{F'_P(T, P)}{P}$$

can be found uniquely without the indefinite term $\varphi(T)$.

In conclusion, it should be emphasized that investigating thermodynamic systems with the aid of thermodynamic functions is presently the most convenient means of solving concrete thermodynamic problems. The method was elaborated by J. Willard Gibbs. Some supplementary features of the method will be considered below in Sec. 24.

Problems

1. Find the quantity of heat liberated (absorbed) in a dielectric placed in an isothermal field with intensity E (see Sec. 16).

Solution. Select as independent variables T and E (V = const). Passing over from the internal energy U [see formula (16.3)] to Gibbs' potential $\Phi = U - TS - \frac{VED}{4\pi}$, we find that

$$d\Phi = -S\,dT - \frac{V}{4\pi} D\,dE.$$

Integrating this expression at T = const and using the relationship $D = \varepsilon(T)\,E$, we find

$$\Phi(T, E) = \Phi(T, 0) - \frac{V}{8\pi}\varepsilon E^2.$$

Since $S = -\left(\frac{\partial\Phi}{\partial T}\right)_E$, we obtain

$$S(T, E) = S(T, 0) + \frac{V}{8\pi}\varepsilon'(T)\,E^2,$$

whence we have

$$Q_T = T[S(T, E) - S(T, 0)] = \frac{VT\varepsilon'(T)\,E^2}{8\pi}.$$

For nonpolar dielectrics (ε = const) $Q_T = 0$; for polar dielectrics $\varepsilon(T) = 1 + \frac{A}{T}$, $\varepsilon'(T) = -\frac{A}{T^2}$ and $Q_T = -\frac{VAE^2}{8\pi T}$. The negative sign at Q_T indicates that heat is liberated and not absorbed. A graphic physical interpretation of this effect can easily be given by departing from molecular ideas. After the field is applied, work is being performed on the dielectric. At the same time, the potential energy of the dipoles decreases, since they are oriented parallel to the field. For this reason the kinetic energy, and the temperature along with it, should increase. Since the process occurs at T = const, the liberated heat must then be absorbed by a thermostat.

2. Show that for an equilibrium radiation Gibbs' potential equals zero.
3. What can be said about the equation of state of a system for which the Gibbs potential equals zero?

Answer. $\left(\frac{\partial P}{\partial V}\right)_T = 0$, $P = f(T)$.

4. A tensile force f is applied to a rod having an initial length l_0. Find the quantity of heat liberated (absorbed) by the rod. Solve the problem with the aid of free energy $F(T, l)$ and

by means of the Gibbs potential $\Phi(T, f)$.

Answer. $Q_T = \alpha T l_0 f \left(1 + \frac{f}{2E\sigma}\right) \approx \alpha T l_0 f$.

20. Thermodynamics of Plasma

This section is devoted to the thermodynamics of a highly ionized gas in which the most of particles have an electric charge (electrons and ions). The microscopic theory of plasma, based on statistical physics, will be covered in Secs. 49 and 66. It should be emphasized that substances in the plasma state are rather abundant in the universe surrounding us—the substance of the stars and the ionospheres of planets are examples of plasma. On earth we encounter plasma in studying gas discharges, flames, blast waves and also in connection with the design and construction of magneto-hydrodynamic (MHD) generators and thermonuclear reactors.

The particles of high-temperature plasma with temperatures of the order of 10^5 K and above emit many quanta, as a consequence of which radiant energy constitutes an important part of the energy of plasma. For a rough (order-of-magnitude) estimate of the temperature at which the kinetic energy can be compared with the radiant energy, it can be assumed that at this temperature the radiation pressure $\frac{\sigma T^4}{3}$ becomes comparable to the gas-kinetic pressure in the plasma, whence follows the estimate $T \sim (P/\sigma)^{1/4}$. At a pressure ranging from 10^{-4} to 10^{-3} mmHg, this gives a temperature in the range between 10^4 and 10^5 K. In this section we limit ourselves to the treatment of low-temperature plasma, ignoring the role played by radiation. As will be shown in Sec. 66, compared with the expression for the internal energy of an ideal gas, the formula for the internal energy of rarefied plasma contains an additional term in the form $\Delta U = -AN^{3/2}T^{1/2}V^{1/2}$ (A = const), associated with the existence of Coulomb interactions between plasma particles. The fact that this additional term is negative is explained by the fact that the attraction forces prevail over the repulsive forces. This in turn is associated with the fact that each ion is surrounded in the plasma by a "cloud" of charges of opposite sign.

The total internal energy per mole is

$$U = U_{id} + \Delta U = C_V T - \frac{A}{T^{1/2}V^{1/2}}. \tag{20.1}$$

We obtained the expression for the internal energy in variables T, V (instead of the natural variables S, V). In accordance with the general principles outlined in Sec. 19, we must turn now to the description of the thermodynamic properties of plasma with the aid of the thermodynamic function in variables T, V, namely, free

energy F. Let us use for this purpose the Gibbs-Helmholtz equation and the relation following from it:

$$F = -T \int \frac{U}{T^2} dT + \varphi(V) T, \tag{20.2}$$

where $\varphi(V)$ is an arbitrary function of volume.

We face, however, the difficulty mentioned in Sec. 19. Expression (20.1) including the internal energy of an ideal gas cannot be extrapolated to cover the region $T \to 0$ and the Nernst heat theorem cannot be used to determine $\varphi(V)$. Integration of Eq. (20.2) leads to the expression

$$F(T, V) = -C_V T \ln T - \frac{2A}{3T^{1/2}V^{1/2}} + \varphi(V) T. \tag{20.3}$$

which is invalid at $T \to 0$. The function $\varphi(V)$ can nevertheless be defined with the aid of passing to the limit as $V \to \infty$ at $T = \text{const}$, since for very rarefied plasma the expression $-C_V T \ln T + \varphi(V) T$ must coincide with that for the free energy of an ideal gas (the correction for the Coulomb interaction vanishes in the limit). Consequently, from Eq. (20.3) we obtain

$$F = F_{\text{id}} - \frac{2}{3} \frac{A}{T^{1/2}V^{1/2}}, \tag{20.4}$$

whence, using formulae $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $P = -\left(\frac{\partial F}{\partial V}\right)_T$ we obtain the expression for the entropy

$$S = S_{\text{id}} - \frac{1}{3} \frac{A}{T^{3/2}V^{1/2}}, \tag{20.5}$$

and the equation of state

$$P = P_{\text{id}} - \frac{1}{3} \frac{A}{T^{1/2}V^{3/2}} \tag{20.6}$$

for rarefied plasma. Differentiating formula (20.5), we find the heat capacity C_V of plasma:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = (C_{\text{id}})_V + \frac{1}{2} \frac{A}{T^{3/2}V^{1/2}}. \tag{20.7}$$

Formula (20.6) shows the pressure in plasma to be lower than that in an ideal gas which, like the minus sign of the correction ΔU, is explained by the predominance of attraction forces between ions in plasma. Formula (20.7) shows that the heat capacity of plasma exceeds that of an ideal gas. This stems from the fact that the heat added to plasma at $V = \text{const}$ is expended not only to increase the kinetic energy of particles, but also to raise the potential energy of the interaction forces between plasma particles.

For plasma the difference $C_P - C_V$ can be found by formula (11.23):

$$C_P - C_V = -\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} = R\frac{\left(1+\frac{A}{6RT^{3/2}V^{1/2}}\right)^2}{1-\frac{A}{2RT^{3/2}V^{1/2}}},$$

or, accurate to infinitesimals of the order of $\frac{A}{RT^{3/2}V^{1/2}}$,

$$C_P - C_V = R\left(1+\frac{5}{6}\frac{A}{RT^{3/2}V^{1/2}}\right). \tag{20.8}$$

Finally, let us find the change in temperature for an adiabatic process occurring in plasma. According to (11.12),

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V = -\frac{P}{(C_{\mathrm{id}})_V}\frac{1+\frac{A}{6RT^{3/2}V^{1/2}}}{1+\frac{A}{2(C_{\mathrm{id}})_V T^{3/2}V^{1/2}}}.$$

In particular, for a monoatomic gas $(C_{\mathrm{id}})_V = 3R/2$ and accurate to infinitesimals of the first order, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{2P}{3R}\left(1-\frac{1}{6}\frac{A}{RT^{3/2}V^{1/2}}\right). \tag{20.9}$$

Problem

Find the quantity of heat required to heat one mole of plasma at $P = \text{const}$ from temperature T_1 to T_2 (accurate to infinitesimals of the order $A/RT^{3/2}V^{1/2}$ and the work performed by the plasma.

Answer. $Q_P = \frac{5}{2}R\left[1+\frac{8}{15}\frac{AP^{1/2}}{R^{3/2}T_1T_2}\right](T_2-T_1)$,

$$A_P = R\left[1+\frac{1}{3}\frac{AP^{1/2}}{R^{3/2}T_1T_2}\right](T_2-T_1).$$

21. Polyvariant Systems. Magnetostriction and the Piezomagnetic Effect

Let us review the problems dealt with in the preceding sections concerning the thermodynamics of various monovariant systems with one mechanical degree of freedom. The basic thermodynamic identity for an arbitrary monovariant system is generally presented in the form

$$dU = T\,dS - X\,dx, \tag{21.1}$$

or, with the aid of the Jacobian in the form

$$\frac{\partial(T, S)}{\partial(X, x)} = 1, \tag{21.2}$$

where X is referred to as the generalized force and the quantity x is called the generalized coordinate (for rod $X = -f$, $x = l$; for a magnetic material $X = -H$, $x = M$, etc.).

It should be noted that for polyvariant systems the second law of thermodynamics, stating that the expression $\delta Q/T$ is a total differential, is, strictly speaking, not a postulate, but is partly a corollary of the well-known mathematical theorem stating that a linear differential expression in two variables, $dU + X\,dx$, always has an integrating divisor. The postulate that we introduce in thermodynamics is that this integrating divisor is identified with temperature.

We can also compile for an arbitrary monovariant system an array of thermodynamic coefficients

$$\begin{vmatrix} \left(\frac{\partial X}{\partial x}\right)_T & \left(\frac{\partial x}{\partial T}\right)_X & \left(\frac{\partial T}{\partial X}\right)_x \\ \left(\frac{\partial S}{\partial T}\right)_x & \left(\frac{\partial T}{\partial x}\right)_S & \left(\frac{\partial x}{\partial S}\right)_T \\ \left(\frac{\partial S}{\partial T}\right)_X & \left(\frac{\partial T}{\partial X}\right)_S & \left(\frac{\partial X}{\partial S}\right)_T \\ \left(\frac{\partial S}{\partial X}\right)_x & \left(\frac{\partial X}{\partial x}\right)_S & \left(\frac{\partial x}{\partial S}\right)_X \end{vmatrix} \tag{21.3}$$

and express 9 coefficients in terms of the three coefficients that can be most readily measured or found in statistical physics, and chosen as independent variables. The definition of free energy $F = U - TS$ remains valid for arbitrary monovariant systems and the expressions for the heat content (enthalpy) and for the Gibbs potential are generalized in the obvious manner:

$$W = U + Xx, \quad \Phi = U - TS + Xx.$$

Let us now consider systems with several mechanical, nonthermal degrees of freedom, the so-called *polyvariant systems*, for which the expression for the elementary work has the form

$$\delta A = \sum_{i=1}^{n} X_i\,dx_i, \tag{21.4}$$

where X_i = generalized force conjugate to the ith generalized coordinate x_i;

n = number of mechanical degrees of freedom.

The principle of energy is, as before, described by the equation

$$dU = \delta Q - \delta A = \delta Q - \sum_{i=1}^{n} X_i\,dx_i. \tag{21.5}$$

Just as for monovariant systems, we can also formulate the temperature principle and the entropy principle for polyvariant sys-

tems. In this case the conditional temperature τ and the conditional entropy σ are functions of the generalized coordinates x_i and of the generalized forces X_i. However, the symmetry between the description of the state of a system in terms of variables P and V and the τ-σ description used for polyvariant systems vanishes, since instead of one pair P, V there exist n pairs of mechanical parameters X_i, x_i, compared to the single thermal degree of freedom for the polyvariant system (one pair of conjugate thermal quantities τ, σ). It is, therefore, expedient to introduce into the theory of polyvariant systems the relationship $\delta Q = T\,dS$ as a postulate. Particular emphasis should be placed on the fact that for polyvariant systems the statement that the expression $dU + \sum_{i=1}^{n} X_i\,dx_i$ has an integrating divisor is no longer a trivial corollary of mathematical theorems, but is a true postulate, according to which for reversible processes the expression

$$\frac{\delta Q}{T} = \frac{dU + \sum_{i=1}^{n} X_i\,dx_i}{T} \tag{21.6}$$

is a total differential.

The main thermodynamic identity takes the form

$$dU = T\,dS - \sum_{i=1}^{n} X_i\,dx_i, \tag{21.7}$$

The condition for the right-hand side of equation (21.7) to be a total differential of the function $U(S, x_1, x_2, \ldots, x_n)$ is the validity of the following relations:

$$\frac{\partial(T, S)}{\partial(X_i, x_i)} = 1 \quad (i = 1, 2, \ldots, n) \tag{21.8}$$

$$\frac{\partial(X_j, x_j)}{\partial(X_i, x_i)} = -1 \quad (i \neq j = 1, 2, \ldots, n). \tag{21.9}$$

Thus, instead of the single equation $\frac{\partial(T, S)}{\partial(X, x)} = 1$ for a monovariant system, the basic thermodynamic identity yields in the case of an n-variant system $n + \frac{n(n-1)}{2} = \frac{n(n+1)}{2}$ equations (21.8) and (21.9).

The expression for free energy $F = U - TS$ remains the same for polyvariant systems. The heat content W and the thermodynamic potential Φ are determined by formulae

$$W = U + \sum_{i=1}^{n} X_i x_i, \quad \Phi = U - TS + \sum_{i=1}^{n} X_i x_i = F + \sum_{i=1}^{n} X_i x_i.$$

It should be noted that the Legendre transformation can be applied to U or F for not all generalized coordinates, but only for a part of them, adding to U or F the term $\sum_{i=1}^{m} X_i x_i$ $(m < n)$.

We then have at our disposal a number of new thermodynamic functions, the natural variables for which will be the partly generalized forces X_i $(i = 1, \ldots, m)$ and the partly generalized coordinates x_i $(i = m + 1, m + 2, \ldots, n)$. These functions have no special names, but they are sometimes convenient to apply.

Let us consider by way of a simple example a bivariant system—a rod placed in a magnetic field. The expression for work is

$$\delta A = -f\,dl - H\,dM, \tag{21.10}$$

i.e. we have

$$X_1 = -f, \quad x_1 = l, \quad X_2 = -H, \quad x_2 = M.$$

The equations

$$\frac{\partial (T, S)}{\partial (X_1, x_1)} = 1, \quad \frac{\partial (T, S)}{\partial (X_2, x_2)} = 1 \tag{21.11}$$

will again give the previously obtained results—the expressions for the temperature variation following adiabatic stretching of the rod with an additional condition of constant magnetizing, or for the demagnetizing of the rod with its length remaining constant. To consider the physical effects that are of interest to us, it is necessary to pass over from the variables l, M to the variables f and H. For this purpose the heat content W^* is introduced:

$$W^* = U^* - fl - HM, \quad dW^* = T\,dS - l\,df - M\,dH. \tag{21.12}$$

The conditions for the right-hand side to be a total differential at S = const is the equation

$$\left(\frac{\partial l}{\partial H}\right)_{S, f} = \left(\frac{\partial M}{\partial f}\right)_{S, H}. \tag{21.13}$$

The derivative on the left-hand side of Eq. (21.13) describes the adiabatic magnetostriction: deformation of the rod (elongation or contraction) upon a change in the magnetic field. The derivative on the right-hand side of Eq. (21.13) is associated with the adiabatic piezomagnetic effect—the effect of magnetizing (demagnetizing) the rod when it is acted upon by a tensile (compressive) force. By analogy, introducing Gibbs' potential $\Phi^* = U^* - TS - fl - HM$, we obtain from the expression

$$d\Phi^* = -S\,dT - l\,df - M\,dH, \tag{21.14}$$

the expression

$$\left(\frac{\partial l}{\partial H}\right)_{T,f}=\left(\frac{\partial M}{\partial f}\right)_{T,H} \tag{21.15}$$

relating isothermal magnetostriction and the isothermal piezomagnetic effect. Expressions (21.13) and (21.15) without any analysis of the internal (molecular) mechanism of the phenomena indicate that these effects are closely related. Magnetostriction and piesomagnetic effect can exist only simultaneously, i.e. if for a certain rod $\left(\frac{\partial M}{\partial f}\right)_{S,H}=0$, then also $\left(\frac{\partial l}{\partial H}\right)_{S,f}=0$ (similarly for $T=$ const).

Further, relationships (21.13) and (21.15) indicate that the directions of the two effects are related. If an increase in the tensile force is followed by a greater magnetizing of the rod $\left[\left(\frac{\partial M}{\partial f}\right)_{S,H}>0\right]$, then the rod elongates upon an increase in the field intensity $\left[\left(\frac{\partial l}{\partial H}\right)_{S,f}>0\right]$, and vice versa. Substances of the two types exist in nature.

The other two conditions following from Eq. (21.12),

$$\left(\frac{\partial T}{\partial H}\right)_{S,f}=-\left(\frac{\partial M}{\partial S}\right)_{H,f}$$

and

$$\left(\frac{\partial T}{\partial f}\right)_{S,H}=-\left(\frac{\partial l}{\partial S}\right)_{H,f},$$

describe already known effects: cooling upon adiabatic demagnetizing (Sec. 15) and a change in rod temperature upon adiabatic extension (Sec. 14).

The other two conditions stemming from Eq. (21.14),

$$\left(\frac{\delta Q}{\delta f}\right)_{T,H}=T\left(\frac{\partial S}{\partial f}\right)_{T,H}=T\left(\frac{\partial l}{\partial T}\right)_{f,H}=l_0\alpha T,$$

$$\left(\frac{\delta Q}{\delta M}\right)_{T,f}=T\left(\frac{\partial S}{\partial H}\right)_{T,f}=T\left(\frac{\partial M}{\partial T}\right)_{f,H}=HT\chi'_{\mathrm{m}},$$

relate the thermal effect upon deformation and magnetizing with the coefficient of linear expansion and the derivative of the magnetic susceptibility respectively.

One more interesting example of a bivariant system is that of a substance placed simultaneously in an electric and a magnetic field. Determine the heat content W^* by formula $W^*=U^*-HM-pE$. We have

$$dW^*=T\,dS-M\,dH-p\,dE. \tag{21.16}$$

By analogy, for Gibbs' potential $\Phi^*=U^*-TS-HM-pE$ we find

$$d\Phi^*=-S\,dT-M\,dH-p\,dE. \tag{21.17}$$

In addition to the already known relations, from formulae (21.16) and (21.17) we arrive at the following total-differential requirements:

$$\left(\frac{\partial M}{\partial E}\right)_{H,S}=\left(\frac{\partial p}{\partial H}\right)_{E,S}, \quad \left(\frac{\partial M}{\partial E}\right)_{H,T}=\left(\frac{\partial p}{\partial H}\right)_{E,T} \tag{21.18}$$

Formulae (21.18) may turn out to be trivial identities of the form $0 = 0$. If this, however, is not so, then these formulae predict a certain relation between these crossing effects: magnetizing of a substance in an electric field and polarization of a substance in a magnetic field.

These effects may evidently occur in polar dielectrics (paramagnetic materials), if the directions of the dipole and magnetic moments in the molecules are correlated, and also in crystals of nonpolar dielectrics (diamagnetic materials), if the directions of the easiest polarization and of the easiest magnetizing are correlated. In crystals these effects have actually been detected and studied both theoretically and by experiment (see [4]).

Problem

Find the relation between electrostriction and the piezoelectric effect.

Answer. $\left(\frac{\partial l}{\partial E}\right)_{S,f}=\left(\frac{\partial p}{\partial f}\right)_{S,E}, \quad \left(\frac{\partial l}{\partial E}\right)_{T,f}=\left(\frac{\partial p}{\partial f}\right)_{T,E}.$

CHAPTER II

SYSTEMS WITH VARIABLE AMOUNT OF MATTER. PHASE TRANSITIONS

22. Systems with Variable Amount of Matter. The Chemical Potential

So far we have been concerned with systems containing a constant quantity of matter. Let us turn now to thermodynamic systems in which the quantity of matter may change. Examples of such systems are bodies undergoing various chemical transformations (in which case the quantity of a given chemical compound is variable), or systems in which phase transitions take place (melting, crystallization, evaporation, the transition from one crystalline modification into another, etc.)—in this case the variable is the quantity of the substance in a definite phase.

The internal energy of such a variable-mass system depends, evidently, not only on its own natural variables, S and V, but also on the quantity of substance, which we shall characterize by the number of moles N. It follows that

$$dU = T\,dS - P\,dV + \mu\,dN, \tag{22.1}$$

where the quantity μ has the dimension of energy per mole and is referred to as the *chemical potential* of a substance. The chemical potential is specified by the formula

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{22.2}$$

Let us subdivide all thermodynamic quantities into *extensive* (additive) and *intensive*. We include in the first class those quantities that increase in proportion to N with an increasing amount of substance in the system, all other conditions being equal. Quantities in this class obviously include the volume of a substance V and the internal energy U, for which we have

$$V = N\tilde{V}, \quad U = N\tilde{U}, \tag{22.3}$$

where $\tilde{V}$ and $\tilde{U}$ are respectively the volume and the internal energy of one mole. In contrast to this, quantities such as temperature T and pressure P do not change with increasing dimensions of the system and so are classified as intensive quantities. By virtue of formula $dS = \frac{\delta Q}{T}$ entropy is also an additive quantity—the entropy of an equilibrium system is equal to the sum of the entropies of its individual parts, and so we can introduce the concept of molar

entropy $\tilde{S}$, related to the total entropy as follows:

$$S = N\tilde{S}. \tag{22.4}$$

Finally, by virtue of formulae

$$F = U - TS, \quad W = U + PV, \quad \Phi = U - TS + PV$$

all the thermodynamic potentials are extensive quantities, and we can introduce molar quantities $\tilde{F}$, $\tilde{W}$, $\tilde{\Phi}$. It is clear that all the molar quantities, the molar volume $\tilde{V}$, the molar entropy $\tilde{S}$, the molar internal and free energies $\tilde{U}$, $\tilde{F}$, the molar enthalpy $\tilde{W}$, etc. are intensive quantities.

Note that molar thermodynamic functions depend on T, P and on the molar arguments $\tilde{V} = V/N$, $\tilde{S} = S/N$, i.e. we have

$$U(S, V, N) = N\tilde{U}\left(\frac{S}{N}, \frac{V}{N}\right), \quad F(T, V, N) = N\tilde{F}\left(T, \frac{V}{N}\right), \tag{22.5}$$

$$W(S, P, N) = N\tilde{W}\left(\frac{S}{N}, P\right), \quad \Phi(T, P, N) = N\tilde{\Phi}(T, P).$$

We return now to the chemical potential and note that by virtue of the definitions of the functions F, W, Φ the term $\mu\, dN$ will be present in the differentials of all thermodynamic functions:

$$dU = T\, dS - P\, dV + \mu\, dN, \quad dF = -S\, dT - P\, dV + \mu\, dN, \tag{22.6}$$

$$dW = T\, dS + V\, dP + \mu\, dN, \quad d\Phi = -S\, dT + V\, dP + \mu\, dN,$$

whence

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V} = \left(\frac{\partial F}{\partial N}\right)_{T, V} = \left(\frac{\partial W}{\partial N}\right)_{S, P} = \left(\frac{\partial \Phi}{\partial N}\right)_{T, P}. \tag{22.7}$$

The relationships (22.5) show the chemical potential to be most simply related to the thermodynamic potential, whose arguments, except for N, are simply the intensive quantities T and P; thus

$$\left(\frac{\partial \Phi}{\partial N}\right)_{T, P} = \mu(T, P) = \tilde{\Phi}(T, P) = \frac{\Phi}{N}, \tag{22.8}$$

i.e. the chemical potential is a thermodynamic potential referred to one mole of substance. Thus the differential of μ is expressed by the formula

$$d\mu = -\tilde{S}\, dT + \tilde{V}\, dP. \tag{22.9}$$

It should be noted that a system with a variable amount of substance is a particular case of a bivariant system having, in addition to the mechanical coordinate V, one more special coordinate—the number of moles N for which the chemical potential μ is the conjugate generalized force.

Consider the differential of the internal energy

$$dU = T\,dS - P\,dV + \mu\,dN. \tag{22.10}$$

The conditions necessary for the right-hand side of Eq. (22.10) to be a total differential can be written in the form

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}, \quad \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{N,V},$$

$$\left(\frac{\partial P}{\partial N}\right)_{S,V} = -\left(\frac{\partial \mu}{\partial V}\right)_{S,N}.$$

Passing over to Jacobians, we have

$$\begin{aligned}
&\frac{\partial(T, S)}{\partial(V, S)} = \frac{\partial(P, V)}{\partial(V, S)} \text{ at } N = \text{const},\\
&\frac{\partial(T, S)}{\partial(N, S)} = \frac{\partial(N, \mu)}{\partial(N, S)} \text{ at } V = \text{const},\\
&\frac{\partial(P, V)}{\partial(N, V)} = \frac{\partial(\mu, N)}{\partial(N, V)} \text{ at } S = \text{const},
\end{aligned} \tag{22.11}$$

or

$$\begin{aligned}
&\frac{\partial(T, S)}{\partial(P, V)} = 1 \text{ at } N = \text{const},\\
&\frac{\partial(T, S)}{\partial(\mu, N)} = -1 \text{ at } V = \text{const},\\
&\frac{\partial(P, V)}{\partial(\mu, N)} = 1 \text{ at } S = \text{const}.
\end{aligned} \tag{22.12}$$

Treating in a similar way the differentials of free energy, heat content (enthalpy) and thermodynamic potential, in addition to Eqs. (22.10) through (22.12) we obtain

$$\frac{\partial(P, V)}{\partial(\mu, N)} = 1 \text{ at } T = \text{const}, \tag{22.13}$$

$$\frac{\partial(T, S)}{\partial(\mu, N)} = -1 \text{ at } P = \text{const}. \tag{22.14}$$

By way of example let us express the derivative $\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$ in terms of easily measured quantities. With the aid of formula (22.13) we get

$$\begin{aligned}
\left(\frac{\partial N}{\partial \mu}\right)_{T,V} &= \left[\frac{\partial(N, V)}{\partial(\mu, V)}\right]_T = \left[\frac{\partial(N, V)}{\partial(N, P)}\frac{\partial(N, P)}{\partial(P, V)}\frac{\partial(P, V)}{\partial(\mu, V)}\right]_T\\
&= \left(\frac{\partial V}{\partial P}\right)_{N,T}\left(\frac{\partial P}{\partial \mu}\right)_{V,T}\left[\frac{\partial(N, P)}{\partial(\mu, N)}\right]_T\\
&= -\left(\frac{\partial V}{\partial P}\right)_{N,T}\left(\frac{\partial P}{\partial \mu}\right)_{V,T}\left(\frac{\partial P}{\partial \mu}\right)_{N,T}.
\end{aligned}$$

Being an intensive quantity, the chemical potential is independent both of the number of moles and of the volume, and so, by virtue of formula (22.9), we obtain

$$\left(\frac{\partial P}{\partial \mu}\right)_{V,T} = \left(\frac{\partial P}{\partial \mu}\right)_{N,T} = \frac{1}{\tilde{V}} = \frac{N}{V}, \tag{22.15}$$

whence

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial V}{\partial P}\right)_{N,T} \frac{N^2}{V^2}.$$

Problem

Prove the formula $\mu(T, P) = \tilde{\Phi}(T, P) = \Phi(T, P)/N$, beginning with the definitions

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial W}{\partial N}\right)_{S,P}.$$

23. The Increase in Entropy in Equalization Processes. The Gibbs Paradox

So far we have been studying equilibrium thermodynamic systems and equilibrium processes. Thermodynamics, however, also allows important conclusions to be made concerning the direction in which non-equilibrium processes for which the initial and intermediate states are not equilibrium ones operate. In particular, these processes include all *equalization processes*, i.e. processes in the course of which a closed system, consisting of two or more parts, each of which is in an equilibrium state, but between which there is no equilibrium, comes into a completely equilibrium state. Let us consider by way of example several such processes. It will be shown that if an equalization process is realized in a heat-insulated system, $\delta Q = 0$, the entropy of this system does not remain constant, as it would have been for an equilibrium adiabatic process, but increases.

Equalization of Temperature. Two bodies at temperatures T_1 and T_2 ($T_1 > T_2$) are brought into contact, with the whole system composed of these two bodies being heat-insulated. Suppose that upon the elapse of a certain time interval a quantity of heat δQ ($\delta Q_1 = -\delta Q$) is released by the first body, while the second body receives the same quantity of heat δQ ($\delta Q_2 = \delta Q$). If the process of heat transfer were reversible (proceeded at an infinitely small temperature difference), the entropy of the bodies would have changed by $dS_1 = -\delta Q/T_1$ and $dS_2 = \delta Q/T_2$ respectively. Since, however, the entropy of each body is a function of its state, then the change in entropy cannot depend on the manner in which the amount of heat δQ was removed from the body, in a reversible or irreversible way;

it depends only on the quantity of heat. This is why the expressions $dS_1 = -\delta Q/T_1$, $dS_2 = \delta Q/T_2$ remain valid also for a real irreversible process, while for the variation in the total entropy we find

$$dS = dS_1 + dS_2 = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1}\right) > 0.$$

Equalization of Pressure. A fixed piston in a heat-insulated cylinder separates two volumes of gas at equal temperature but different pressures P_1 and P_2 ($P_1 > P_2$). The piston is released and the process of pressure equalization begins. The real irreversible process is said to be an isoenergetic one, inasmuch as the system does not perform work on external bodies, nor is heat added to it from the outside. To make it possible to use the formula $dS = \delta Q/T$, let us replace this real process with an imaginary isoenergetic equilibrium process. For this purpose, imagine that the piston is acted upon from the right by an external force smaller by an infinitely small fraction (per unit piston area) than the difference $P_1 - P_2$. The pressure force acting upon the piston will thus be almost balanced by the external force and the gas will undergo reversible expansion. Since the initial and final states are the same for the real irreversible and the imaginary reversible processes (they are on one constant-energy line), the entropy variation is the same for the two processes. As the gas undergoes expansion by dV in the left-hand part of the cylinder during the imaginary process, the system performs work equal to $(P_1 - P_2)\,dV$ against the external force. Since the process is isoenergetic, it is accompanied by the addition of heat $\delta Q = \delta A = (P_1 - P_2)\,dV$ and, consequently, by an increase in entropy by

$$dS = \frac{\delta Q}{T} = \frac{P_1 - P_2}{T}\,dV > 0.$$

Thus, in the processes under consideration the equalization of temperature and pressure is accompanied by an increase in entropy.

Let us emphasize here the following fact of fundamental importance: inasmuch as in the two examples considered above the system consisting of two bodies is heat-insulated, no entropy is added during these processes from the outside, but is generated inside the system. This means that when a system undergoes an irreversible process of temperature and pressure equalization, there are acting in the system internal sources of entropy. As the state of equilibrium is being approached these sources become exhausted and once the system comes into a state of equilibrium, cease to generate entropy.

Let us study from this point of view two more non-equilibrium processes that have already been considered above.

The Gay-Lussac Process. An equivalent reversible process must proceed at a constant internal energy:

$$dU = T\,dS - P\,dV = 0,$$

whence

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T} > 0, \tag{23.1}$$

i.e. during the irreversible expansion of gas into a vacuum entropy increases.

It is helpful to compare a real Gay-Lussac process with an imaginary or fictitious process with the aid of the following table.

Table

Real Gay-Lussac process	Imaginary process
Non-equilibrium	Equilibrium
Adiabatic $\delta Q = 0$	Non-adiabatic $\delta Q \neq 0$
Non-isentropic $dS \neq \delta Q/T$	Non-isentropic $dS \neq \delta Q/T$
Isoenergetic $dU = 0$	Isoenergetic $dU = 0$

The Joule-Thomson Process. An equivalent reversible process occurs at a constant heat content (enthalpy)

$$dW = T\,dS + V\,dP = 0,$$

whence

$$\left(\frac{\partial S}{\partial P}\right)_W = -\frac{V}{T} < 0. \tag{23.2}$$

Further, since in the Joule-Thomson process the gas forces its way through a porous plug into a space at a lower pressure, the entropy in this process also increases.

Let us compare the Joule-Thomson process with the imaginary process used to replace it with the aid of the following table. In

Table

Real Joule-Thomson process	Imaginary process
Non-equilibrium	Equilibrium
Adiabatic $\delta Q = 0$	Non-adiabatic $\delta Q \neq 0$
Non-isentropic $dS \neq \delta Q/T$	Non-isentropic $dS = \delta Q/T$
Isoenthalpic $dW = 0$	Isoenthalpic $dW = 0$

order to examine one more example of an increase in entropy, it is first necessary to extend formula (4.6) of the molar entropy of a perfect gas,

$$\widetilde{S} - \widetilde{S}_0 = \frac{R}{\gamma - 1} \ln\left(\frac{T\widetilde{V}^{\gamma-1}}{T_0\widetilde{V}_0^{\gamma-1}}\right),$$

to cover the case of an arbitrary quantity of gas. [Entropy is denoted by $\tilde{S}$ and volume by $\tilde{V}$, to emphasize that formula (4.6) pertains to one mole of gas.]

Owing to the additivity property of entropy and volume, substitute in formula (4.6) $\tilde{S} = S/N$ and $\tilde{V} = V/N$ (S and V are the entropy and volume of N moles of gas). The formula for entropy may be rewritten to read

$$S = \frac{NR}{\gamma - 1} \ln (TV^{\gamma - 1}) + A, \tag{23.3}$$

where the constant A depends on the number of moles

$$A = N \left[\tilde{S}_0 - \frac{R}{\gamma - 1} \ln (T_0 \tilde{V}_0^{\gamma - 1}) \right] - NR \ln N = BN - RN \ln N. \tag{23.4}$$

The constant B, depending only on the intensive quantities $\tilde{S}_0$, $\tilde{V}_0$, T_0, is independent of the number of moles.

Let us look now at the question of calculating the entropy of a mixture of two different perfect gases. Let a vessel of volume V

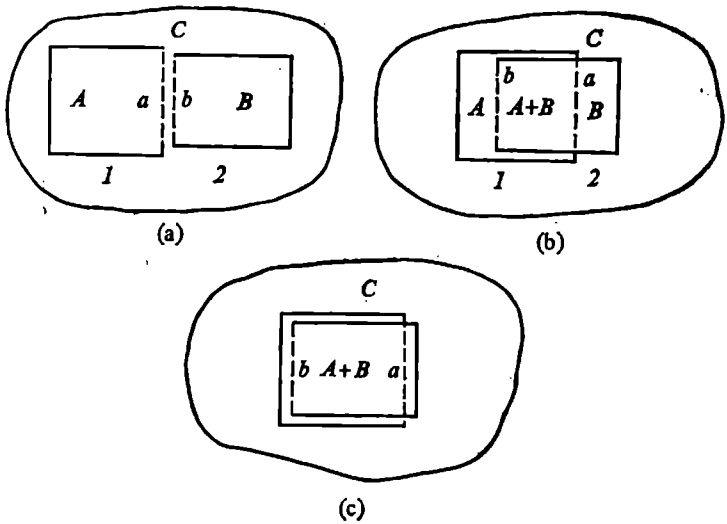


FIG. 33

contain N_1 moles of the first gas and N_2 moles of the second gas. Following Gibbs, let us carry out mentally an experiment showing that this mixture can be obtained from the basic components in a reversible way without performing work and adding heat. Imagine two cylinders *1* and *2* with equal volumes V (Fig. 33), freely entering each other without friction and surrounded by a heat-insulating

enclosure C. The initial position of the two cylinders is depicted in Fig. 33(a). Cylinder *1* is filled with gas A and cylinder *2* with gas B. The right wall a of cylinder *1* is permeable to the molecules of gas B and impermeable to the molecules of gas A, while the left wall b of cylinder B is impermeable to gas B and permeable to gas A. Let us slowly insert vessel *2* into *1* [Fig. 33(b)]. The space to the left of the partition b contains gas A, the space ba is filled with the mixture of gases A and B, and the space to the right of the partition contains gas B. Note that vessel B is being displaced without performing work, since the left and right walls of vessel *2* are exposed to the same pressure, equal to the partial pressure P_2 of gas B. Gas A permeates freely through partition b, exerting no pressure on it, and the resultant force acting on vessel *2* equals zero. At the end of this process the volume V of the combined cylinders [Fig. 33(c)] will be filled with a mixture of gases A and B, with the temperature of the gases not changing inasmuch as the gases undergo an isentropic ($A = 0$, $Q = 0$) mixing. Since the process is also reversible, the entropy of the gases does not change and the entropy of the mixture is expressed by

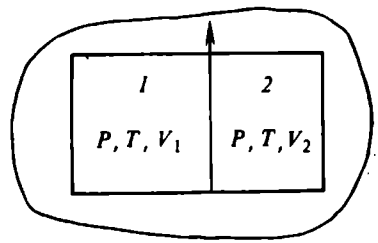


FIG. 34

$$S(T, V) = S_1(T, V) + S_2(T, V). \tag{23.5}$$

In this way we came to *Gibbs' theorem* stating that to calculate the entropy of a mixture it is necessary to add the entropies of the mixture components, assuming the components to be at the same temperature and that they occupy the entire volume of the mixture.

Consider one more example of an adiabatic non-equilibrium process accompanied by an increase in entropy.

Interdiffusion of Two Gases. A heat-insulated vessel (Fig. 34), separated by a partition into two parts with volumes V_1 and V_2, contains two different perfect gases at the same pressure and temperature. According to formulae (23.3) and (23.4) their entropies equal respectively

$$\begin{aligned} S_1 &= \frac{N_1 R}{\gamma_1 - 1} \ln (T V_1^{\gamma_1 - 1}) + B_1 N_1 - R N_1 \ln N_1, \\ S_2 &= \frac{N_2 R}{\gamma_2 - 1} \ln (T V_2^{\gamma_2 - 1}) + B_2 N_2 - R N_2 \ln N_2. \end{aligned} \tag{23.6}$$

After the partition is removed, isothermal mixing of the gases takes place ($\Delta A = 0$, $\Delta Q = 0$, $\Delta U = 0$). At the end of the process,

according to (23.5) the entropy of the mixture is expressed by

$$S=\frac{N_1R}{\gamma_1-1}\ln\left[T\left(V_1+V_2\right)^{\gamma_1-1}\right]+B_1N_1-RN_1\ln N_1$$
$$+\frac{N_2R}{\gamma_2-1}\ln\left[T\left(V_1+V_2\right)^{\gamma_2-1}\right]+B_2N_2-RN_2\ln N_2. \quad (23.7)$$

The change in entropy $\Delta S = S - S_1 - S_2$ is expressed by

$$\Delta S=N_1R\ln\frac{V_1+V_2}{V_1}+N_2R\ln\frac{V_1+V_2}{V_2}>0. \quad (23.8)$$

Thus, this irreversible adiabatic process—the equalization of concentrations—is also accompanied by an increase in entropy.

Formula (23.8) leads to the so-called *Gibbs paradox*: since the quantities characterizing the individual properties of the two gases, γ_1 and γ_2, do not appear on the right-hand side of formula (23.8), it might seem that entropy increases even when two portions of the same gas are mixed. In this case, however, the removal of the partition does not result in any change in state and the entropy cannot change.

Within the framework of thermodynamics the Gibbs paradox is explained by the fact that the formulae (23.5) and (23.7) pertain only to a mixture of two different gases. In the case of two volumes of the same gas the partitions *a* and *b* in the mentally conducted experiment (see Fig. 33) are either impermeable to the two portions of the gas, or permeable to them. In either case the displacement of vessel *B* does not result in mixing of the two portions of gas, but the compression of the gas does take place, accompanied by the performance of work on the gas and, if the process occurs in a thermostat, by the removal of heat. Thus, entropy decreases during the process and Gibbs' theorem becomes inapplicable. For this reason the entropy of any number of moles of a perfect gas must be computed by formulae (23.3), (23.4) without resorting to formula (23.5). Equations (23.3), (23.4), derived on the basis that entropy is an extensive quantity, do not lead, naturally, to any paradoxes. This is vividly clear if these formulae are rewritten to read

$$S=N\left\{\frac{R}{\gamma-1}\ln\left[\left(\frac{V}{N}\right)^{\gamma-1}T\right]+B\right\}.$$

If the number of moles N and volume V are increased α times without changing the temperature, then entropy will increase in the same proportion.

The examples considered above show that entropy increases in equalization processes occurring in a closed system. This law can be proved more comprehensively only on the basis of atomic and molecular concepts, and this proof will be discussed in Sec. 91.

Thus, we accept, so far as a postulate, the statement that the entropy of an isolated system undergoing equalization processes increases, $dS > 0$. The final result of an equalization process is a completely equilibrium state. In the case of small deviations from equilibrium the gradients of all the system parameters are also small, and all processes occurring close to the state of equilibrium acquire the nature of slow, approximately equilibrium processes. Consequently, in the state of equilibrium $dS = 0$. From this follows the important conclusion that as the state of equilibrium is approached, the entropy of an isolated system increases and reaches its maximum value in the state of equilibrium.

The law of increase in entropy in an isolated system is of paramount importance. This law can be said to be, in a way, more comprehensive from the physical viewpoint than the law of conservation of energy. In fact, when applied to an isolated system, the law of conservation of energy states that the transition from state *I* to state *II* is only possible provided $U_1 = U_2$—the energy of the system in the initial state is equal to that in the final state. But if this condition is satisfied, then, from the energy viewpoint, the reverse process of the passing of the system from state *II* to state *I* is equally possible.

For instance, from the point of view of the law of conservation of energy the following processes are equally possible.

1. Processes of heat leakage from a body at a higher temperature to a body at a lower temperature and the reverse process (if the energy balance is observed).
2. A process of gradual deceleration and stopping due to friction of a body moving over a rough surface (with the kinetic energy of the body being converted into the energy of random molecular motion) and the reverse process (the energy of random molecular motion being converted into the energy of orderly motion of the body), in the course of which the body at rest cools off somewhat, but as a result begins to move.
3. Expansion of a gas into a vacuum (the Gay-Lussac process) and the reverse process of spontaneous compression of the gas.
4. Interdiffusion of two different gases and the spontaneous separation of the gas mixture.

The number of similar examples could, naturally, be multiplied.

The law of increase in entropy allows, for heat-insulated systems, the forward processes in items 1 through 4, associated with an increase in (generation of) entropy, but prohibits the reverse processes involving a decrease in entropy*.

* A. Sommerfeld cites in his book [1] the figurative note made by Robert Emden: "In the huge manufacture of natural processes, the principle of entropy occupies the position of manager, for it dictates the manner and method of the whole business, whilst the principle of energy merely does the book-keeping, balancing credits and debits".

Thus, the basic meaning of the law of increase in entropy consists in establishing the existence of irreversible processes, in particular, of all equalization processes. All these processes become reversible when the system approaches the state of equilibrium and entropy attains its maximum value.

It should be noted in concluding this section (digressing from its main topic, the increase in entropy) that we have widened to some extent the framework of equilibrium thermodynamics and have considered some non-equilibrium processes. The method that has been used in the discussion involved the replacement of a real non-equilibrium process by an equivalent imaginary equilibrium process.

There is one more method of studying non-reversible processes, applied to cases when the initial and final states of a system are completely equilibrium states or in equilibrium with respect to some of the system's parameters. This method resembles to a certain extent the black box problem of cybernetics: we have a certain device with an unknown internal structure, a black box, and the problem is to learn how to relate input and output signals. By analogy, the thermodynamics of equilibrium processes fail to give us any data on the development of an irreversible process. We can, however, make use of any equations that are valid for the initial and final (equilibrium) states, in particular, of the energy principle, equation of state, etc.

Let us consider by way of illustration the following problem: a gas forces its way through a small opening into a vessel that was originally evacuated. The atmospheric temperature and pressure, T_0 and P_0, are assumed to be constant. The problem is to find the temperature of the gas in the vessel at the moment the pressures inside and outside the vessel become equal. The temperature relaxation time is far greater than the pressure equalization time and beginning with $T > T_0$ the state of the gas in the vessel that is non-equilibrium with respect to temperature can be assumed to be a metastable state during the time that measurements are taken. The gas is assumed to be perfect.

The answer to the problem is provided by the energy principle. Since the process of heat transfer has no time to terminate during the time the gas flows into the vessel, then the change in the internal energy of the gas already in the vessel, $nC_V (T - T_0)$, equals the work done by the external force (atmosphere) on the gas. If the gas filling the vessel occupied volume V_0 in the atmosphere, this (isobaric) work is equal to $P_0V_0 = nRT_0$, whence the equation $C_V (T - T_0) = RT_0$, $T = \frac{C_V+R}{C_VT_0} = \gamma T_0$. It is interesting to note that we made no use of the pressure equalization requirement and, consequently, any small amount of gas entering the vessel acquires the temperature γT_0. The subsequent amounts of the gas that flow into the vessel

are heated to lower temperatures, since they are being forced into the vessel by the pressure $P_0 - P$, where P is the pressure inside the vessel; though they compress and heat the portions of the gas which entered previously. The result shows these effects to compensate each other, and that the increase in temperature is independent of the amount of gas entering the vessel.

Problem

A vessel of volume $2V$ is placed inside a heat-insulated vessel and is separated into two equal parts by a partition. The two halves of the vessel contain gas at the same temperature T_0 and at different pressures P_1 and P_2 ($P_1 > P_2$). A hole (with dimensions that are large compared with the free-path length) is opened up in the partition, and equalization of the pressures takes place. Find the common pressure P, the temperatures of the gas in the two halves of the vessel, T_1 and T_2 (the observation time is small compared with the heat-transfer time), and the number of moles of the gas that passed from one half of the vessel into the other, ΔN.

Answer. $P = \frac{1}{2}(P_1 + P_2)$, $\frac{T_1}{T_0} = \left(\frac{P_1 + P_2}{2P_1}\right)^{\frac{\gamma-1}{\gamma}}$,

$$\frac{T_2}{T_0} = \left[2 - \left(\frac{P_1 + P_2}{2P}\right)^{\frac{1-\gamma}{\gamma}}\right]^{-1},$$

$$\Delta N = \frac{P_1 V}{RT_0}\left[1 - \left(\frac{P_1 + P_2}{2P_1}\right)^{1/\gamma}\right].$$

Hint. Consider the mass of gas that fills the first half of the vessel fully after the hole is opened, and apply to that mass of the equation of the steady-state adiabatic process.

24. Extrema of Thermodynamic Functions

Let us make sure now that just like entropy, other thermodynamic functions also have extrema.

Consider first of all an irreversible process occurring in a system that is not heat-insulated, and an amount of heat δQ is added to this system or removed from it. This process can be mentally visualized as a sequence of two processes, a process during which the system acquires a state of equilibrium without supply of heat and its entropy increases, $dS_1 > 0$, and the following reversible process involving addition or removal of heat, during which entropy increases by $\delta Q/T = dS_2 > 0$ if heat is added, and $dS_2 < 0$, if heat is removed from the system.

Combining the two relationships, we obtain the inequality

$$dS = dS_1 + dS_2 \geqslant \frac{\delta Q}{T}, \quad \delta Q \leqslant T\,dS, \tag{24.1}$$

with the equality sign being valid only for equilibrium reversible processes. Using now the energy principle,

$$dU = \delta Q - P\,dV,$$

we obtain the inequality replacing in the case of irreversible processes the basic thermodynamic identity:

$$dU \leqslant T\,dS - P\,dV. \tag{24.2}$$

Using the definitions of free energy $F = U - TS$, heat content (enthalpy) $W = U + PV$ and thermodynamic potential $\Phi = U - TS + PV$, we obtain from (24.2) the inequalities

$$dF \leqslant -S\,dT - P\,dV, \tag{24.3}$$

$$d\Phi \leqslant -S\,dT + V\,dP, \tag{24.4}$$

$$dW \leqslant T\,dS + V\,dP. \tag{24.5}$$

Let us first turn to the corollaries stemming from inequalities (24.3) and (24.4). Consider processes occurring in a thermostat ($T = \text{const}$) under two different supplementary conditions: $V = \text{const}$ and $P = \text{const}$. Inequalities (24.3) and (24.4) give

$$dF < 0 \quad \text{at} \quad V = \text{const}, \quad T = \text{const}, \tag{24.6}$$

$$d\Phi < 0 \quad \text{at} \quad P = \text{const}, \quad T = \text{const}. \tag{24.7}$$

Thus, when an irreversible process approaches equilibrium at $V = \text{const}$ and $T = \text{const}$, the free energy decreases, and at $P = \text{const}$ and $T = \text{const}$ the thermodynamic potential diminishes. All processes become equilibrium ones in the neighbourhood of the state of equilibrium, and we have

$$dF = 0 \quad \text{at} \quad V = \text{const}, \quad T = \text{const}, \tag{24.8}$$

$$d\Phi = 0 \quad \text{at} \quad P = \text{const}, \quad T = \text{const}. \tag{24.9}$$

It follows from the foregoing that when a system for which $V = \text{const}$, $T = \text{const}$ is in the state of equilibrium, the free energy acquires a minimum value, $F = F_{\min}$, and in a system for which $P = \text{const}$, $T = \text{const}$, the thermodynamic potential is minimum, $\Phi = \Phi_{\min}$.

Let us make now the following important remark. Inequalities (24.2) through (24.5) make sense only in the assumption that the parameters P, V, T, S have definite values for the non-equilibrium states of the system as well. The fact that entropy has also definite value for non-equilibrium states of the system stems from the very

statement of the entropy increase law. It will be shown below, in Secs. 35 and 63, that the formulae of statistical physics actually determine the entropy of any equilibrium or non-equilibrium state of a system. As to the parameters P, V, T, we shall limit ourselves to the consideration of such non-equilibrium states, in which these parameters also have definite values. In particular, there are no temperature and pressure gradients in these states. It follows from this that the foregoing concerns the systems that are characterized, in addition to the parameters P, V, T, S, by one or more variable parameters ξ_i and the thermodynamic potentials U, F, W, Φ depend, in addition to their own natural arguments, on the parameters ξ_i. In a state of thermodynamic equilibrium these parameters acquire the values $\xi_i^{(0)}$ that must be found from the conditions of minimum free energy F at $T = \text{const}$, $V = \text{const}$ or minimum thermodynamic potential Φ at $T = \text{const}$.

Examples of such systems, for instance, are systems consisting of several chemical substances reacting with each other, or systems consisting of several phases, in which melting, boiling and other processes can take place. The role of parameters ξ_i is then played by the numbers determining the composition of a system, for instance, the number of moles of all chemical components or of all phases of the system.

Consider now a body that is in contact with the surroundings, assuming that the body is not yet in thermal equilibrium with the surroundings, so that the temperature T_0 and the pressure P_0 of the surroundings differ from the temperature T and pressure P of the body. Consider the energy and volume of the surroundings to be so large that no matter what processes the body undergoes, T_0 and P_0 can be assumed to be constant. The surroundings and the body placed in it form a closed system, in consequence of which we have

$$\Delta U = -\Delta U_0 = -T_0 \Delta S_0 + P_0 \Delta V_0 = -T_0 \Delta S_0 - P_0 \Delta V \tag{24.10}$$

(all quantities with the subscript "0" pertain to the surroundings and the quantities without a subscript to the body). On the other hand, in the process of equalization the total entropy must increase, $\Delta S_0 + \Delta S \geqslant 0$, whence we find the inequality

$$\Delta (U - T_0 S + P_0 V) \leqslant 0. \tag{24.11}$$

In a particular case $T = T_0 = \text{const}$, $V = \text{const}$ we get again the inequality $dF \leqslant 0$ and the condition for thermodynamic equilibrium $F = F_{\min}$. In the case $T = T_0 = \text{const}$, $P = P_0 = \text{const}$ we obtain the inequality $d\Phi \leqslant 0$, and the equilibrium condition $\Phi = \Phi_{\min}$. In the general case, however, when $T \neq T_0$, $P \neq P_0$, Eq. (24.11) shows that in the process of temperature and pressure equalization

the potential $\Phi^* = U - T_0S + P_0V$ decreases, and in the state of equilibrium $\Phi^* = \Phi^*_{\min}$.

Let us illustrate the foregoing by two simple examples.

1. A cylinder, separated by an easily sliding piston into two compartments of volume V_1 and V_2 containing N_1 and N_2 moles of a perfect gas, is placed into a thermostat at a temperature T. The piston is at first fixed and the pressures in the compartments are P_1 and P_2, not equal to each other. Then the piston is released, and the system attains a state of equilibrium. According to (24.8), the condition of equilibrium requires the free energy to assume a minimum value. The free energies F_1 and F_2 are expressed by

$$F_i = U_i - TS_i = N_i C_{V_i} T - \frac{N_i RT}{\gamma_i - 1} \ln (TV_i^{\gamma_i - 1}) - TA_i$$

$$= f_i(T) - N_i RT \ln V_i,$$

whence

$$F = f(T) - N_1 RT \ln V_1 - N_2 RT \ln (V - V_1).$$

The free energy of a non-equilibrium system, in addition to its fixed arguments T, V, depends on the parameter V_1, by which F has to be minimized. The required equilibrium condition is

$$\frac{\partial F}{\partial V_1} = -\frac{N_1 RT}{V_1} + \frac{N_2 RT}{V - V_1} = 0,$$

i.e. the equality of pressures in the compartments, $P_1 = P_2$, with $V_2/V_1 = N_2/N_1$.

2. Replace in the preceding example the left-hand wall with a second easily sliding piston, acted upon by the constant thermostat pressure P_0. At first the pistons are fixed, and in the compartments the pressure $P_1 \neq P_2 \neq P_0$. Then the pistons are released, and the process of attaining equilibrium occurs. According (24.11), the criterion of equilibrium requires the free potential $\Phi^* = U - TS + P_0V$ to assume a minimum value; by analogy with the preceding example, the potential is equal to

$$\Phi^* = f(T) + N_1 RT \ln P_1 + N_2 RT \ln P_2 + P_0 \left(\frac{N_1 RT}{P_1} + \frac{N_2 RT}{P_2} \right)$$

(we used formula

$$S = \frac{NR}{\gamma - 1} \ln \left(\frac{T^\gamma}{P^{\gamma - 1}} \right) + \text{const}$$

and the equality $V_i = N_i RT/P$). In addition to its fixed arguments T and P_0, the potential Φ^* depends on the parameters P_1 and P_2, which should be used to minimize the potential. We have

$$\frac{\partial \Phi^*}{\partial P_i} = \frac{N_i RT}{P_i} - \frac{P_0 N_i RT}{P_i^2} = 0, \quad P_i = P_0, \quad V_i = \frac{N_i RT}{P_i}.$$

Let us turn now to considering non-equilibrium processes occurring at $S = \text{const}$ and two supplementary conditions: either $V = \text{const}$, or $P = \text{const}$. It should be emphasized that in distinction to processes with $T = \text{const}$ that can readily be realized in a thermostat, irreversible processes with $S = \text{const}$ can only be realized in rather artificial conditions. In fact, irreversible processes are characterized by the fact that entropy is being produced in the system, and to maintain the entropy constant, we should have available a cybernetic device with feedback that would remove exactly the amount of entropy (heat) required. For this reason the conditions

$$U = U_{\min} \text{ at } S = \text{const}, \quad V = \text{const}$$

and

$$W = W_{\min} \text{ at } S = \text{const}, \quad P = \text{const},$$

that can be obtained from inequalities (24.2) and (24.5), have no practical significance and they are mentioned here pursuing methodological considerations only.

The difference between the potentials U and W, on the one hand, and the potentials F and Φ, on the other hand, noticed above, is based on the following fundamental fact.

The potentials U and W have neither sources, nor sinks in the system and they can be "added" to the system from the outside or "removed" from it to the surrounding medium. As far as the internal energy is concerned, this fact is obvious, since the internal energy can change only upon addition or removal of heat and after positive or negative work is performed.

For heat content this stems from the fact that this function can be considered to be the energy of some "extended" system. For example, the total energy U_{tot} of a gas filling a cylinder closed with a piston of cross-sectional area σ bearing a load of mass m is expressed by the formula

$$U_{\text{tot}} = U + mgh = U + P\sigma h = U + PV = W$$

(h is the height of the column of gas above the piston).

Consequently, the functions U and W are uniquely specified both in the equilibrium and non-equilibrium states of the system, and they do not change in non-equilibrium equalization processes: at $\delta Q = 0$ and $V = \text{const}$ for the internal energy, at $\delta Q = 0$ and $P = \text{const}$ for the heat content (enthalpy). Of course, in the case of non-equilibrium states, the internal energy U, being a single-valued function of state, can no more be considered as single-valued function of the parameters S and V, and the heat content, being a single-valued function of state, cannot be considered as a single-valued function of the parameters S and P (these parameters, generally, have no definite values in non-equilibrium states).

For the functions of state U and W the absence of internal sources manifests itself in the fact that, in addition to the inequalities

$$dU \leqslant T\,dS - P\,dV, \quad dW \leqslant T\,dS + V\,dP,$$

valid for them are the equalities

$$dU = \delta Q - P\,dV, \quad dW = \delta Q - P\,dV + d\,(PV),$$

indicating that the quantities U and W can change only at the expense of added (removed) heat and performed work. For W this is the work done on the "extended" system, including the work spent in lifting the load placed on the piston, $d\,(PV) = d\,(mgh)$.

In contrast to this, for the functions F and Φ there exist negative sources (sinks) that function inside a system undergoing irreversible processes, since the definitions of the functions include entropy:

$$F = U - TS, \quad \Phi = U + PV - TS.$$

The existence of the sinks follows from the fact that in these processes entropy has positive sources inside the system. As a result, in contrast to the functions U and W, F and Φ are not determined uniquely in non-equilibrium states by the values of T and V or T and P but depend on other parameters. It is precisely this fact that explains why these functions possess the above-mentioned extrema that the functions U and W fail to possess.

Let us consider in concluding this section a state of thermodynamic equilibrium in the presence of a time-independent applied potential field.

In the presence of a field the expression for the differential of Gibbs' potential will obviously include one more term, $\mathcal{U}\,(x, y, z)\,dN$ (where the term $\mathcal{U}\,(x, y, z)$ is the potential energy in the external field referred to one mole):

$$d\Phi = -S\,dT + V\,dP + [\mu + \mathcal{U}\,(x, y, z)]\,dN. \qquad (24.12)$$

Formula (24.12) gives

$$\left(\frac{\partial \Phi}{\partial N}\right)_{T, P} = \mu\,(T, P) + \mathcal{U}\,(x, y, z), \qquad (24.13)$$

whence for the total potential Φ we find

$$\Phi = \int [\mu\,(T, P) + \mathcal{U}\,(x, y, z)]\,dN, \qquad (24.14)$$

where dN is the number of moles in a small element of volume dV.

The condition of minimum for Φ in respect to the small variations $\delta\,(dN)$ with the supplementary condition $\int \delta\,(dN) = 0$ (the normalization condition) leads to the equality

$$\int [\mu\,(T, P) + \mathcal{U}\,(x, y, z) - \lambda]\,\delta\,(dN) = 0$$

(λ is a Lagrangian multiplier), whence

$$\mu(T, P) + \mathcal{U}(x, y, z) = \lambda = \text{const}. \qquad (24.15)$$

Since the other condition of equilibrium is $T = \text{const}$, it follows from Eq. (24.15) that in the presence of a field pressure changes from point to point. Calculating the gradient of the left-hand and right-hand sides of Eq. (24.15), we obtain

$$\left(\frac{\partial \mu}{\partial P}\right)_T \nabla P + \nabla \mathcal{U}(x, y, z) = 0,$$

or

$$\tilde{V} \nabla P = \mathbf{F}(x, y, z) = -\nabla \mathcal{U}(x, y, z). \qquad (24.16)$$

Equality (24.16) shows how in the equilibrium state pressure depends on the coordinates in the presence of an external field. In particular, for an ideal gas placed in a uniform gravitational field $\mathcal{U}(x, y, z) = Mgz$ we obtain (M = molar mass)

$$\frac{RT}{P}\frac{dP}{dz} = -Mg,$$

whence, integrating, we obtain the *barometric formula*

$$P = P_0 e^{-\frac{Mgz}{RT}}.$$

Problems

1. A vessel of volume $2V$ containing an ideal gas is separated into two equal parts by an easily sliding piston, weighing $P_0\sigma$ (where σ is the cross-sectional area of the piston). The vessel is arranged horizontally in a thermostat at temperature T. The pressure in the two halves of the vessel is equal to P. The vessel is turned through 90° around its centre of gravity. Find the new volumes and pressures, V_1, V_2, P_1, P_2, the change in the entropy ΔS_1 and the quantity of heat removed to the thermostat, ΔQ. (Give an elementary solution of the problem and a solution based on the condition of minimum for a corresponding thermodynamic function.) The vessel is turned again through 90° around its new centre of gravity. Find the new changes in entropy and the removed heat, ΔS_2 and ΔQ_2.

Answer. After the first turn

$$V_1 = V[1 + x - \sqrt{1 - x^2}], \quad V_2 = V[1 - x + \sqrt{1 - x^2}],$$

$$P_1 = \frac{P}{1 + x - \sqrt{1 + x^2}}, \quad P_2 = \frac{P}{1 - x + \sqrt{1 + x^2}},$$

$$\Delta S_1 = \frac{PV}{T} \ln [2x(\sqrt{1 + x^2} - x)] < 0,$$

$$\Delta Q_1 = P_0 V(x - \sqrt{1 + x^2}) < 0, \quad x = \frac{P}{P_0} \left(\Delta Q_1 \neq T \Delta S_1\right).$$

After the second turn $\Delta S_2 = -\Delta S_1$, $\Delta Q_2 = 0$.

Hint. The free energy including the potential energy of the piston, as a function of one of the volumes V_1 or V_2 (non-equilibrium parameter), has a minimum value in the state of equilibrium. The parameters V_1, V_2, P_1, P_2 can also be found from the equations $P_2 - P_1 = P_0$, $V_1 + V_2 = 2V$ and from the equation of state.

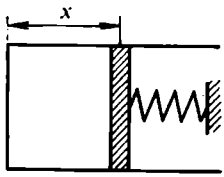


FIG. 35

2. What thermodynamic function of a system gas-spring (Fig. 35) is at its minimum in the state of equilibrium? The springed piston is placed into a thermostat at temperature T. The spring constant is $\varkappa(T)$, the distance between the piston and the left-hand wall, when the spring is not stretched, is equal to x_0, and the cross-sectional area of the cylinder is σ.

Find the equilibrium value of x and the gas pressure P from extremum considerations and applying the elementary method*.

Answer. In the state of thermodynamic equilibrium the minimum total free energy of the gas-spring system acquires a minimum value:

$$F = F_{\text{gas}} + \frac{\varkappa (x - x_0)^2}{2}, \quad x = \frac{x_0}{2}\left[1 + \sqrt{1 + \frac{4RT}{\varkappa x_0^2}}\right].$$

25. Thermodynamic Inequalities

The condition of thermodynamic equilibrium at constant temperature and pressure requires the thermodynamic potential to assume a minimum value. This means that if in the equilibrium state the increments of the parameters S and V (P = const, T = const) are δS and δV, the increment of the thermodynamic potential $\delta\Phi$, must be non-negative at any values of δS and δV. This requires that the coefficients at δS and δV become zero, since the terms containing δS and δV to the first power change their sign as the signs of δS and δV change. For small deviations from equilibrium the sufficient condition of minimum for the potential Φ is the requirement for the differential of the second order to be positive. Consider this condition for a homogeneous system.

* The problem was suggested by G. L. Kotkin.

For a small deviation from the equilibrium state at $P = \text{const}$ and $T = \text{const}$ we have

$$\delta\Phi = \delta(U - TS + PV) = \left(\frac{\partial U}{\partial S}\right)_V \delta S + \left(\frac{\partial U}{\partial V}\right)_S \delta V + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_V (\delta S)^2 + 2\frac{\partial^2 U}{\partial S\,\partial V}\delta S\,\delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)_S (\delta V)^2\right] - T\,\delta S + P\,\delta V, \quad (25.1)$$

where all derivatives of the internal energy U are taken in the equilibrium state, in which

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P, \quad (25.2)$$

and only terms of the second order remain in expression (25.1).

From Eq. (25.2) we also find

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V},$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S, \quad \frac{\partial^2 U}{\partial S\,\partial V} = \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (25.3)$$

Rewrite inequality (25.1) to read

$$\left(\frac{\partial T}{\partial S}\right)_V (\delta S)^2 + 2\left(\frac{\partial T}{\partial V}\right)_S \delta S\,\delta V - \left(\frac{\partial P}{\partial V}\right)_S (\delta V)^2 > 0. \quad (25.4)$$

With arbitrary δS and δV the conditions of validity of (25.4) are, as is known, the inequalities

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0, \quad (25.5)$$

$$\left(\frac{\partial P}{\partial V}\right)_S < 0, \quad (25.6)$$

$$\left(\frac{\partial T}{\partial V}\right)_S^2 + \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial P}{\partial S}\right)_V + \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial P}{\partial V}\right)_S < 0. \quad (25.7)$$

The first inequality gives

$$C_V > 0. \quad (25.8)$$

Inequality (25.8) has a simple physical meaning. Let a temperature fluctuation take place in some fixed volume, for instance, compared with the equilibrium temperature T_0, the temperature increased by ΔT. Then at $C_V < 0$, by virtue of the definition $\left(\frac{\partial U}{\partial T}\right)_V = C_V$, the internal energy of the volume under consideration would decrease. This would cause heat transfer from the surrounding sections to the section under consideration and would, consequently, cause

a further rise in temperature. Similarly, temperature fluctuation resulting in a decrease in temperature in some region at $C_V < 0$ would not die out and the temperature would tend to get lower. Thus, a state with $C_V < 0$ would be absolutely unstable with respect to small temperature fluctuations—a catastrophic heating of a substance would take place in some regions and cooling to the absolute zero in other regions.

Inequality (25.7) can be rewritten to read

$$\frac{\partial(T, P)}{\partial(S, V)} = \frac{\partial(T, P)}{\partial(T, V)} \frac{\partial(T, V)}{\partial(S, V)} = \frac{T}{C_V} \left(\frac{\partial P}{\partial V}\right)_T < 0$$

and by virtue of (25.8), it gives

$$\left(\frac{\partial P}{\partial V}\right)_T < 0. \tag{25.9}$$

With a homogeneous system in steady states both isothermal compression and adiabatic compression [see (25.6)] lead to an increase in pressure and vice versa.

The visual meaning of inequality (25.6) or (25.9) is quite clear: in a steady state a gas must behave as a spring, i.e. a decrease in the volume of some mass of the gas must be accompanied by an increase in pressure inside this mass and vice versa. In the process small gas density fluctuations will die out. On the contrary, at $\left(\frac{\partial P}{\partial V}\right)_T > 0$ (for instance, on the rising branch of van der Waals' isotherm, see Sec. 12) density fluctuations do not die out but increase. Let, for instance, a fluctuation compression of a substance occur in some region. At $\left(\frac{\partial P}{\partial V}\right)_T > 0$ it will be accompanied by a decrease in pressure inside the mass, and the external pressure will continue to compress it till a drop of liquid forms. On the contrary, the region in which a fluctuation decrease in density took place will be expanded by the increased internal pressure till the region passes into a normal state of a gas with $\left(\frac{\partial P}{\partial V}\right)_T < 0$. In other words, if such a state would appear for a moment, the point lying on the rising branch of van der Waals' isotherm (Fig. 21) would instantaneously "fall down" on the isotherm-isobar ACE, representing the two-phase state of substance. Thus, states with $\left(\frac{\partial P}{\partial V}\right)_T < 0$ are absolutely unstable with respect to small density fluctuations or to separation of substance into two phases.

26. Phase Equilibrium. First-Order Phase Transitions

So far we have been considering the thermodynamic behaviour of physically homogeneous systems. Let us turn now to studying systems comprising several phases in equilibrium with one another.

By a *phase* is meant a physically homogeneous part of a system differing in physical properties from other parts of the system and separated from them by a well-defined boundary. Examples of two-phase systems are a liquid and its saturated vapour, a liquid and a crystal, two crystalline modifications of the same substance in contact with each other, etc. It should be noted that in a system whose phases are in equilibrium, a slight variation of external conditions (for instance, an addition or removal of some amount of heat) results in that a certain amount of the substance passes from one phase state into another (fusion, boiling, etc.). That is why, in studying the conditions of phase equilibrium, we consider simultaneously the development of the so-called *phase transitions*.

We shall consider the nature of phase transitions at constant pressures and temperatures. For a two-phase system, in addition to T and P, the thermodynamic potential depends on the number of moles in each phase, N_1 and N_2:

$$\Phi = \Phi(T, P, N_1, N_2), \quad d\Phi = -S\,dT + V\,dP + \mu_1\,dN_1 + \mu_2\,dN_2, \tag{26.1}$$

where

$$\mu_1 = \left(\frac{\partial \Phi}{\partial N_1}\right)_{T, P, N_2}, \quad \mu_2 = \left(\frac{\partial \Phi}{\partial N_2}\right)_{T, P, N_1}$$

are the chemical potentials of the first and second phase respectively, or

$$d\Phi_{T, P} = \mu_1\,dN_1 + \mu_2\,dN_2.$$

Writing down Eq. (26.1), we assume that there are no pressure and temperature gradients in the system, so that we have an equilibrium state with respect to these parameters. Only the numbers of moles N_1 and N_2 may have nonequilibrium values, and we are interested in the way these numbers change in an equalization process.

If a system undergoes equalization, then, as was elucidated in Sec. 24, the thermodynamic potential decreases, $d\Phi < 0$. But $N_1 + N_2 = \text{const}$, $dN_2 = -dN_1$ and, consequently,

$$(\mu_1 - \mu_2)\,dN_1 \leqslant 0, \tag{26.2}$$

whence it follows that $dN_1 \leqslant 0$ at $\mu_1 \geqslant \mu_2$ and, on the contrary, $dN_1 \geqslant 0$ at $\mu_1 \leqslant \mu_2$, i.e. mass flows from the phase with a higher chemical potential to the phase with a lower chemical potential.

In the state of thermodynamic equilibrium the thermodynamic potential of the system Φ has a minimum value, $d\Phi = 0$, whence it follows that the two phases come to equilibrium at $\mu_1 = \mu_2$.

Thus, for a mass flow from one phase into the other the chemical potential plays the same role as the temperature does for heat transfer or pressure for gas flow in corresponding equalization processes.

Heat flows from points at a higher temperature to points at a lower temperature and heat transfer ceases as soon as temperatures equalize. Gas flows from points at a higher pressure to points at a lower pressure and the flow of gas ceases upon pressure equalization. Mass flow is directed from a phase with a higher chemical potential to a phase with a lower chemical potential, and mass transfer terminates when the chemical potentials become equal.

It should be noted that when a temperature gradient provokes heat transfer in a substance or when a pressure gradient results in gas flow, it is clear that these flows lead to temperature and pressure equalization, respectively. A direct corollary of inequality (26.2) is the change in the number of moles N_1 and N_2, and the question arises how the transfer of particles from one phase to another can lead to an equalization of the chemical potentials of the phases, μ_1 and μ_2. The answer to this question will be given at the end of this section, after a qualitative consideration of the dependence of the chemical potential on temperature and pressure.

It should be noted that if at a certain moment of time the phases of a two-phase system are not at equilibrium (for instance, $\mu_1 > \mu_2$), but the phases in contact are at the same temperature and pressure, the molecular transfer from the first phase to the second is an irreversible adiabatic process (the two-phase system is assumed to be heat-insulated) that must be accompanied by an increase in entropy.

Let us show that this is really so. The process can be visualized, for instance, in the following way. A closed heat-insulated vessel contains a liquid and unsaturated vapour above it. The absence of equilibrium (the unsaturation of the vapour) is guaranteed by the fact that the film covering the surface of the liquid is impermeable to the molecules of the substance. Then the film is removed and an irreversible process of equalization of the chemical potentials takes place. Following the common interpretation method applied to irreversible processes, let us replace the one considered above by an imaginary slow reversible process of evaporation. We can, for instance, leave the film in place, but assume it to become more and more permeable.

We can apply to the imaginary equilibrium process the basic thermodynamic identity

$$dU_i = T\,dS_i - P\,dV_i + \mu_i\,dN_i$$

($i = 1, 2$, the subscript 1 pertains to the liquid and the subscript 2 to the vapour). Whence the change in total entropy is expressed by

$$dS = dS_1 + dS_2 = \frac{d(U_1+U_2) + Pd(V_1+V_2) - \mu_1\,dN_1 - \mu_2\,dN_2}{T}.$$

Since the imaginary process, just as the real one, is an isoenergetic, $dU_1 = -dU_2$, and an isochoric, $dV_1 = -dV_2$, process, with the

molecules passing only from the first phase into the second, $dN_2 = -dN_1$, we obtain

$$dS = \frac{\mu_1 - \mu_2}{T} dN_2 > 0,$$

since $\mu_1 > \mu_2$, $T > 0$.

Thus, for two coexisting phases of a substance to be at equilibrium, in addition to pressure equality, $P_1 = P_2$, and temperature equality, $T_1 = T_2$, the chemical potentials of the two phases must be equal,

$$\mu_1 (T, P) = \mu_2 (T, P). \tag{26.3}$$

This equation permits in principle to express one of the arguments of the chemical potential in terms of the other, i.e. makes it possible to find the dependence $P = P(T)$ or $T = T(P)$ (for instance, to find the pressure of a saturated vapour as a function of temperature or the melting point as a function of pressure, etc.), and, consequently, the equation can be used to plot on the P-T plane the equilibrium-phase curve. However, to find the equation of the curve $P = P(T)$ in a particular case, we must have the analytical expression for the chemical potentials of both phases.

Not knowing the exact expression for the chemical potentials $\mu_1 (T, P)$, $\mu_2 (T, P)$, we can, however, find the differential equation of the phase-transition curve. Equation (26.3) shows the chemical potential to change continuously when a phase transition takes place. In the general case, however, during a phase transition the derivatives of the chemical potential $\left(\frac{\partial \mu}{\partial T}\right)_P = -\tilde{S}$ and $\left(\frac{\partial \mu}{\partial P}\right)_T = \tilde{V}$ undergo a discontinuity jump, i.e. the molar volume and the molar entropy of the first phase are not equal to the molar volume and the molar entropy of the second phase, $\tilde{V}_1 \neq \tilde{V}_2$, $\tilde{S}_1 \neq \tilde{S}_2$. Such phase transitions are referred to as *phase transitions of the first order*. Since the phase transition, or change of phase, occurs at constant temperature T, then from formula $\delta Q = T\,d\mathrm{S}$ it follows that the discontinuity jump in entropy, $\tilde{S}_2 - \tilde{S}_1$, is related to the molar heat of phase transition λ by formula

$$\lambda = T (\tilde{S}_2 - \tilde{S}_1). \tag{26.4}$$

The assertion that during a first-order phase transition $\tilde{S}_2 \neq \tilde{S}_1$ is equivalent to $\lambda \neq 0$. Thus, first-order phase transitions are accompanied by a jumpwise increase in volume and by absorption or liberation of heat of transition. Examples of phase transitions of this kind are all changes in the state of aggregation (boiling, melting, etc.) and many mutual transformations of crystal modifications of the same substance.

The molar heat of phase transition λ can be calculated not only by formula (26.4), but also in another way. According to the energy

principle, we have

$$\lambda = \tilde{U}_2 - \tilde{U}_1 + \tilde{A} = \tilde{U}_2 - \tilde{U}_1 + P(\tilde{V}_2 - \tilde{V}_1) = \tilde{W}_2 - \tilde{W}_1, \tag{26.5}$$

where $\tilde{A}$ = work done when one mole of a substance changes from one phase to the other;
$\tilde{W}$ = molar enthalpy.

The quantity λ is often referred to as the enthalpy of phase transition (evaporation, boiling, etc.).

Let us derive now the differential equation of the equilibrium-phase curve plotted on a P-T plane.

Let as move along the curve representing a first-order phase transition from one point to another, the second being very close to the first. By virtue of Eq. (26.3), we have

$$d\mu_1(T, P) = d\mu_2(T, P) \tag{26.6}$$

and, making use of formula (22.9), we obtain the differential equation of the phase-transition curve,

$$\frac{dP}{dT} = \frac{\tilde{S}_2 - \tilde{S}_1}{\tilde{V}_2 - \tilde{V}_1}, \tag{26.7}$$

that can be rewritten with the aid of formula (26.4) to read

$$\frac{dP}{dT} = \frac{\lambda}{T(\tilde{V}_2 - \tilde{V}_1)}, \tag{26.8}$$

which is known as the *Clapeyron-Clausius equation*.

It is clear from Eq. (26.8) that when $\lambda > 0$ (phase transition with absorption of heat), $\frac{dP}{dT} > 0$ at $\tilde{V}_2 > \tilde{V}_1$ and, vice versa, i.e. when a phase change is accompanied by an increase in volume, the phase-transition temperature rises with pressure (for instance, boiling of liquid), and when a phase transition involves a decrease in volume, a contrary phenomenon takes place (for instance, melting of ice).

In order to integrate Eq. (26.8) and find the dependence $P(T)$ or $T(P)$ in the explicit form along the phase-transition curve, we must know the equations of state for each phase, $\tilde{V}_1 = f_1(P, T)$ and $V_2 = f_2(P, T)$, and the dependence of the heat of phase transition (latent heat) on temperature. In some particular cases, however, equation (26.8) can be integrated in a simpler way.

Let us consider by way of example a liquid-vapour equilibrium at temperatures low compared to the critical one. In this temperature region $\tilde{V}_2 \gg \tilde{V}_1$ and the vapour is so rarefied, that its molar volume V_2 obeys with sufficient accuracy the equation of state for an ideal

gas, $\tilde{V}_2 = RT/P$. In this region Eq. (26.8) reduces to

$$\frac{dP}{dT} = \frac{\lambda P}{RT^2}.$$

Assuming λ = const and integrating, we find

$$P = P_\infty \exp\left(-\frac{\lambda}{RT}\right), \tag{26.9}$$

where P_∞ is the pressure that the gas would have at $T \to \infty$. In fact, expression (26.9) becomes invalid at $T \sim T_{cr}$.

The Clapeyron-Clausius equation can be used in solving a number of problems involving first-order phase transitions. Let there exist some physical quantity depending on pressure and temperature, A (P, T) (we can take for this quantity the molar volume $\tilde{V}_i$ of any phase, the molar entropy $\tilde{S}_i$ of any phase, the heat capacity C_i, the heat of phase transition λ, etc.). We are interested in the change of this quantity along the equilibrium-phase curve, depending on pressure and temperature. We have the following obvious formulae:

$$\left(\frac{dA}{dP}\right)_\mu = \left(\frac{\partial A}{\partial P}\right)_T + \left(\frac{\partial A}{\partial T}\right)_P \frac{dT}{dP} = \left(\frac{\partial A}{\partial P}\right)_T + \left(\frac{\partial A}{\partial T}\right)_P \frac{T(\tilde{V}_2 - \tilde{V}_1)}{\lambda}, \tag{26.10}$$

$$\left(\frac{dA}{dT}\right)_\mu = \left(\frac{\partial A}{\partial T}\right)_P + \left(\frac{\partial A}{\partial P}\right)_T \frac{dP}{dT} = \left(\frac{\partial A}{\partial T}\right)_P + \left(\frac{\partial A}{\partial P}\right)_T \frac{\lambda}{T(\tilde{V}_2 - \tilde{V}_1)}, \tag{26.11}$$

where $\left(\frac{dA}{dP}\right)_\mu$ and $\left(\frac{dA}{dT}\right)_\mu$ are the derivatives along the equilibrium phase curve.

Consider two examples, illustrating the application of formulae (26.10) and (26.11)

1. Calculate the derivative of the molar heat of phase transition with respect to temperature. According to formula $\lambda = T(\tilde{S}_2 - \tilde{S}_1)$, and making use of formula (26.11), we find

$$\left(\frac{d\lambda}{dT}\right)_\mu = \tilde{S}_2 - \tilde{S}_1 + T\left[\left(\frac{\partial \tilde{S}_2}{\partial T}\right)_P - \left(\frac{\partial \tilde{S}_1}{\partial T}\right)_P\right] + T\left[\left(\frac{\partial \tilde{S}_2}{\partial P}\right)_T - \left(\frac{\partial \tilde{S}_1}{\partial P}\right)_T\right]\frac{\lambda}{T(\tilde{V}_2 - \tilde{V}_1)}.$$

Using $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we obtain

$$\left(\frac{d\lambda}{dT}\right)_\mu = \frac{\lambda}{T} + C_{P_2} - C_{P_1} - \lambda \frac{(\partial \tilde{V}_2/\partial T)_P - (\partial \tilde{V}_1/\partial T)_P}{\tilde{V}_2 - \tilde{V}_1}$$

In particular, at temperatures low compared to the critical temperature, $\tilde{V}_2 = \frac{RT}{P} \gg \tilde{V}_1$ and $\left(\frac{\partial \tilde{V}_2}{\partial T}\right)_P = \frac{R}{P} \gg \left(\frac{\partial \tilde{V}_1}{\partial T}\right)_P$, whence

$$\left(\frac{d\lambda}{dT}\right)_\mu = C_{P_2} - C_{P_1}. \tag{26.12}$$

2. Let us find the compressibility of vapour $\left|\tilde{V}_2^{-1}\left(\frac{d\tilde{V}_2}{dP}\right)_\mu\right|$ along the equilibrium-phase curve. According to (26.10),

$$\left(\frac{d\tilde{V}_2}{dP}\right)_\mu = \left(\frac{d\tilde{V}_2}{dP}\right)_T + \left(\frac{\partial \tilde{V}_2}{\partial T}\right)_P \frac{T(\tilde{V}_2 - \tilde{V}_1)}{\lambda},$$

and at $T \ll T_{cr}$, $\tilde{V}_2 = RT/P$ we have

$$\left(\frac{d\tilde{V}_2}{dP}\right)_\mu = -\frac{RT}{P^2}\left(1 - \frac{RT}{\lambda}\right),$$

whence for the compressibility we obtain

$$\left|\tilde{V}_2^{-1}\left(\frac{d\tilde{V}_2}{dP}\right)_\mu\right| = P^{-1}\left(1 - \frac{RT}{\lambda}\right). \tag{26.13}$$

The temperature $T_0 = \lambda/R$, above which the expression on the right-hand side of Eq. (26.13) would become negative, is rather high. For instance, for water at pressure $P = 1$ atm this temperature is about 5000 K, which considerably exceeds the critical temperature, equal to 647 K. For this reason in the entire temperature region in which formula (26.13) is applicable, the second term represents a small addition to the isothermal compressibility of an ideal gas, equal to P^{-1}.

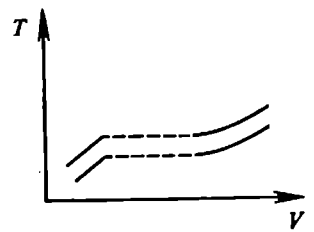


FIG. 36

We have considered the curve of the first-order phase transition plotted on the P-T plane, on which the intensive quantities T and P have no discontinuity jumps. Let us consider qualitatively first-order phase transition depicted on a T-V plane, on which volume undergoes a discontinuity jump when the transition temperature is attained at a given fixed pressure (Fig. 36).

Let us also consider qualitatively a first-order phase transition represented graphically on a plane of two extensive variables, S and V. The thermal and caloric equations of state for each of the two phases are $f_1(P, V, T) = 0$ and $f_2(S, V, T) = 0$. Adding to these equations the equation of the equilibrium-phase curve plotted on the P-T plane, $P = f(T)$, we can eliminate from these equations P and T and find the equation of two curves on the S-V

plane, $S = S_1(V)$ and $S = S_2(V)$, on which the first and second phases, respectively, cease to be stable (Fig. 37). The isobars and isotherms of the first phase terminate on curve *I*. In course of the phase transition the volume and the entropy undergo discontinuity jumps (dotted lines) and the isobars and isotherms of the second phase originate on curve *II*. Between curves *I* and *II* there is the region of forbidden values of S and V.

Let us consider now on P-V and T-S diagrams a first-order liquid-to-vapour phase transition undergone by a van der Waals' gas. As was already mentioned in Sec. 12, van der Waals' equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

describes rather approximately both liquid and gaseous states of a substance. The isotherms of this equation are plotted in Fig. 38. The segment of the curve between points *1* and *2* must describe the

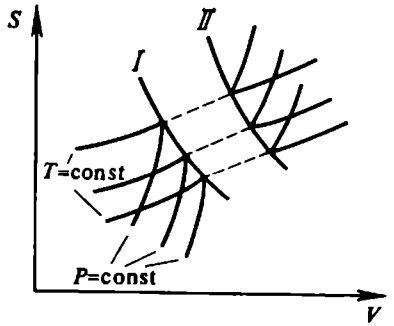


FIG. 37

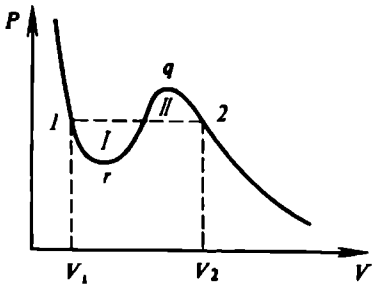


FIG. 38

transition from the liquid into the gaseous phase. Under ordinary conditions, however, a real phase transition does not follow the curve *1rq2*, but is represented by isobar *1-2* (as it should be, since pressure undergoes no discontinuity jump in a phase transition).

Let us prove that the equilibrium-phase equation (26.3) is equivalent to the equal area requirement for areas *I* and *II* in Fig. 38 (Maxwell's equal area rule). In fact, as it was shown in Sec. 6, the work done in an isothermal process is equal to the decrease in the free energy. For the work done along the isotherm *1rq2* we have

$$A_T = \int_{1rq2} P\,dV = \tilde{F}_1 - \tilde{F}_2.$$

On the other hand, the equality of the chemical potentials of a liquid and a gas $\mu_1 = \mu_2$, gives

$$\tilde{F}_1 + P\tilde{V}_1 = \tilde{F}_2 + P\tilde{V}_2,$$

whence we obtain

$$\int\limits_{1rq2} P\,d\tilde{V} = P\,(\tilde{V}_2 - \tilde{V}_1), \tag{26.14}$$

i.e. the integral taken along van der Waals' curve is equal to the area of the rectangle below isobar *1-2* and, consequently, areas *I* and *II* are equal. Thus, on the *P-V* diagram we observe a discontinuity jump in volume, $\tilde{V}_2 - \tilde{V}_1$, the magnitude of which is determined by Maxwell's equal area rule.

Let us consider the transition from the liquid to the gaseous state depicted on the *T-S* plane, where the discontinuity jump of entropy is clearly seen. The isobars of a van der Waals' gas plotted on the *T-S* plane are shown in Fig. 39. The form of these curves can be found only qualitatively, since the entropy of a van der Waal's gas cannot be expressed as a function of *T* and *P* in a finite form. To find the temperatures at which the phase transition and the discontinuity jump of the entropy take place, we must plot the isotherm *1-2*. Let us prove that the position of this isotherm is also determined by Maxwell's equal area rule stating that the areas *I* and *II* must be equal.

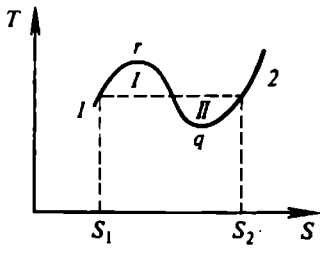


FIG. 39

It is clear from formula (19.3) for the differential of the heat content that in an isobaric process the added heat is equal to the change in the heat content. Thus, integrating along the isobar *1rq2*, for one mole of a gas we have

$$Q = \int\limits_{1rq2} T\,dS = \tilde{W}_2 - \tilde{W}_1.$$

On the other hand, the condition for equality of the chemical potentials of a liquid and a gas, $\mu_1 = \mu_2$, gives

$$\tilde{W}_1 - T\tilde{S}_1 = \tilde{W}_2 - T\tilde{S}_2;$$

comparing the two equalities, we find

$$\int\limits_{1rq2} T\,dS = T\,(\tilde{S}_2 - \tilde{S}_1), \tag{26.15}$$

i.e. the area below isobar *1rq2* equals the area below isotherm *1-2*.

Let us consider qualitatively how the curves $\mu_1\,(T, P)$ and $\mu_2\,(T, P)$ intersect at $T = \text{const}$ or $P = \text{const}$. Since

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \tilde{V} > 0, \quad \left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial \tilde{V}}{\partial P}\right)_T,$$

the curves $\mu_1(P)$ and $\mu_2(P)$ at $T = \text{const}$ have the form as depicted in Fig. 40. The abscissa of the intersection point, P_t, evidently determines the pressure at the phase-transition point at the preset temperature T. Since the equilibrium state corresponds to the minimum value of thermodynamic potential, then at $P > P_t$ the second phase with a smaller molar volume is the stable one, and at $P < P_t$, stable is the first phase with a larger molar volume. The vertical arrows indicate the direction of the phase transition at $P < P_t$ and $P > P_t$.

Thus, a two-phase system responds to an increase in pressure by that the phase with a larger molar volume changes into the phase with a smaller molar volume, which results in a decrease in pressure. This property of the phase transition is a specific manifestation

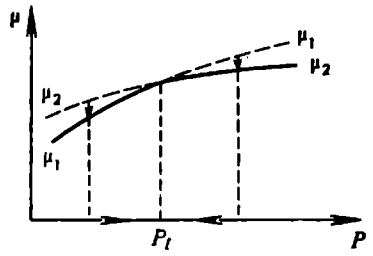


FIG. 40

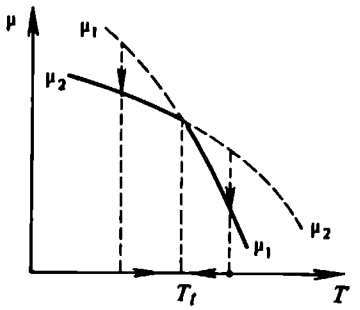


FIG. 41

of the *Le Chatelier principle*—an external action upon a system causes a reaction in it that tends to annul the effect of the external action. Consider the curve representing the dependence $\mu(T)$ at $P = \text{const}$. We have

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -\widetilde{S} < 0, \quad \left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\frac{\widetilde{C}_P}{T} < 0.$$

Thus the curves representing the dependences $\mu_1(T)$ and $\mu_2(T)$ at $P = \text{const}$ are of the form shown in Fig. 41.

In the figure the curve $\mu_1(T)$ runs steeper than the curve $\mu_2(T)$ and, consequently, the molar entropy of the first phase is greater than the molar entropy of the second phase. The abscissa of the point of intersection specifies the temperature of phase transition at the given pressure. The first phase is stable to the right of the transition point, and the second phase—to the left of it (the meaning of the vertical arrows in Fig. 41 is the same as in Fig. 40). It should be noted that an increase in temperature results in a transition from the first phase to the second, with the latent heat of phase

transition being positive, $\lambda = T(\tilde{S}_1 - \tilde{S}_2) > 0$, i.e. the process occurs with heat absorption, which entails a drop in temperature. This is another example illustrating the Le Chatelier principle.

We can now give an answer to the question posed in the beginning of this section, concerning the nature of equalization of the chemical potentials as particles pass over from one phase to the other. It was shown that when the pressure or temperature of a two-phase system deviate from the equilibrium values, P_t and T_t, the transition of particles from one phase to the other results in a smaller deviation (arrows on the abscissa axes in Figs. 40 and 41). This means that the phases are in a stable equilibrium. It can be seen that as pressure P_t or temperature T_t approach their respective equilibrium values, the difference in the chemical potentials, $\mu_1 - \mu_2$, diminishes and becomes zero at the equilibrium point.

Problems

1. Find the heat capacity of a saturated vapour C_μ.

Answer. $C_\mu = C_{P_2} - \left(\frac{\partial V_2}{\partial T}\right)_P \frac{\lambda}{\tilde{V}_2 - \tilde{V}_1} \approx C_{P_2} - \frac{\lambda}{T}$ (the latter equality is valid at $T \ll T_{cr}$). (The subscript 2 pertains to a vapour and the subscript 1 to a liquid.)

2. Find $\left(\frac{\partial V}{\partial T}\right)_\mu$ for a liquid and for a vapour in equilibrium, taking the equation of state for the liquid in the form

$$V_1 = V_0[1 - \gamma P + \alpha(T - T_0)].$$

Answer. Far from the critical point

$$\left(\frac{\partial V_2}{\partial T}\right)_\mu = \frac{R}{P}\left(1 - \frac{\lambda}{RT}\right), \quad \left(\frac{\partial V_1}{\partial T}\right)_\mu = V_0\alpha\left(1 - \frac{\gamma}{\alpha}\frac{\lambda P}{RT^2}\right).$$

3. Find the pressure of a saturated vapour, taking into account the temperature dependence of λ stemming from formula (26.12), $\lambda = \lambda_0 - T\Delta C$ ($\Delta C = C_{P_1} - C_{P_2} > 0$).

Answer. $P = AT^{-\Delta C/R} e^{-\lambda_0/RT}$.

4. How will the pressure of saturated vapour change, if the confining vessel contains air at a partial pressure P ($P/P_{sat} \ll 1$).

Answer. $\Delta P_{sat} \approx \left(\frac{\tilde{V}_1}{\tilde{V}_2}\right) P$.

5. Prove that at $P < P_{cr}$ the isobar of a van der Waals' gas has the form shown in Fig. 39.

Hint. Prove that $\left(\frac{\partial T}{\partial S}\right)_P$ changes its sign twice.

27. Three-Phase Equilibrium. Superheating and Supercooling

When plotted on a P-T plane, the equilibrium curve for the first and second phases is given by the equation

$$\mu_1 (P, T) = \mu_2 (P, T),$$

and the equilibrium curve for the second and third phases—by the equation

$$\mu_2 (P, T) = \mu_3 (P, T).$$

If the two curves intersect at the point P_0, T_0, then at this point the following relationships are valid:

$$\mu_1 (P_0, T_0) = \mu_2 (P_0, T_0) = \mu_3 (P_0, T_0) \qquad (27.1)$$

and, consequently, three phases of a substance coexist in equilibrium at that point. Equations (27.1) permit in principle to find the parameters P_0, T_0 of such a state. The corresponding point on the P-T plane is called the *triple point*.

The equilibrium curves for the first and second, second and third, first and third phases meet at the triple point. So, for instance, for water this diagram of state has the form shown in Fig. 42. For water

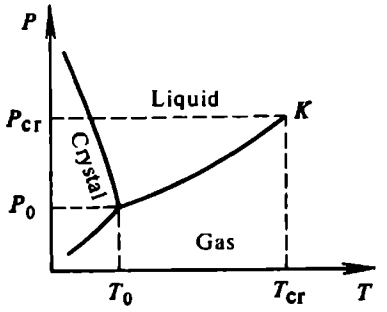


FIG. 42

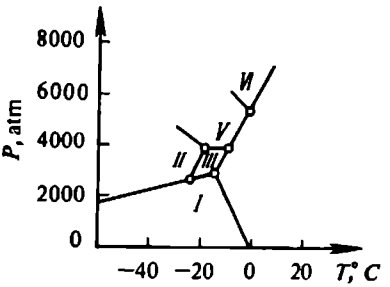


FIG. 43

the parameters of the triple point are $T_0 = 0.0078$ °C, $P_0 = 0.006$ atm. At this temperature and pressure water, ice and water vapour coexist at equilibrium. It is clear from the diagram that at a pressure lower than P_0 ice converts upon heating directly into vapour, without passing through the liquid phase, i.e. sublimates. At a temperature below T_0 ice thaws upon an increase in pressure and when pressure is lowered it sublimates.

The triple point does not necessarily describe equilibrium coexistence of the solid, liquid and gaseous phases of a substance. Most substances have not one but several crystal modifications. Therefore

the region of the solid phase is actually subdivided into a number of subregions. Then the triple point can depict the equilibrium coexistence of two crystal and one liquid phases or of two crystal and one gaseous phases, or, finally, the equilibrium coexistence of three crystal phases.

Figure 43 shows by way of example a more comprehensive diagram of state for water. Five different crystal modifications of ice are denoted by *I* (ordinary ice), *II*, *III*, *V* and *VI*. It is clear from the figure that modifications *II*, *III*, *V*, *VI* are stable at a pressure of several thousand atmospheres. The gaseous state region corresponds to pressures so low that it cannot be shown on the diagram

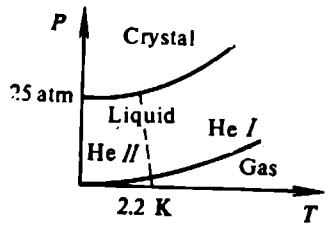


FIG. 44

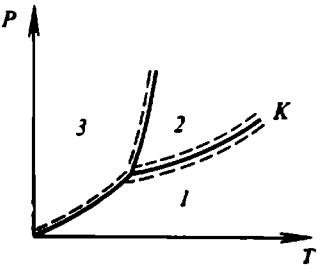


FIG. 45

with the adopted scale. It can be seen from the figure that there are six triple points (the triple point at which ice *I*, water and water vapour are in equilibrium naturally is not shown on the diagram).

For helium the equilibrium coexistence of solid, liquid and vapour phases is quite impossible. The diagram of state for helium is depicted in Fig. 44. The curve separating the regions in which the liquid modifications of helium, He *I* and He *II*, exist is the line of second-order phase transition (see Sec. 28).

Some other specific features of the diagram of state should be pointed out. The equilibrium curve for liquid and vapour phases terminates at the critical point P_{cr}, T_{cr}, at which the difference between the liquid and the gaseous states of the substance vanishes. The equilibrium-phase curve of all substances, except helium, passes through the origin of coordinates. The equilibrium curve separating the liquid and the solid phases has no apparent discontinuity jump and continues to infinity, since the difference between the solid (symmetrical) and liquid (asymetrical) phases cannot vanish.

The regions of metastable states (dotted lines in Fig. 45) adjoin the two-phase equilibrium curves. This means that in region *1*, in which the gaseous state is thermodynamically stable, there can exist under some conditions a liquid in a metastable state, i.e. a superheated liquid. Conversely in region *2*, where the liquid is in a stable state, a vapour can exist under certain conditions in a

metastable state, i.e. a supersaturated vapour. In region *3*, in which the crystal phase of a substance is in a stable state, there can exist under certain conditions a liquid in a metastable state, i.e. a supercooled liquid.

The possible existence of these metastable states is connected with the behaviour of molecules in the thin surface layer separating the two phases. The depth of this layer is of the order of the range of molecular interaction.

A detailed study of the surface layer requires a knowledge of the intermolecular forces, and is a rather complicated matter. It is, however, possible to approach the problem within the framework of thermodynamics in a purely phenomenological way, mentally replacing the surface layer by an infinitely thin boundary surface, or interface, separating the two phases. The interface has been shown experimentally to possess an additional free energy, meaning that to increase the area of the interface by $d\sigma$ at a constant temperature, it is necessary to perform work $\alpha\, d\sigma$, where the quantity α is independent of the area and depends only on the substance of the two phases and on temperature. The quantity α is measured in units of energy divided by area, and is referred to as the *surface tension*. Thus, allowing for boundary effects, the energy of a two-phase system ceases to be additive quantity and is expressed by the formula

$$F = N_1\tilde{F}_1 + N_2\tilde{F}_2 + \alpha\sigma, \tag{27.2}$$

where $\tilde{F}_1$ and $\tilde{F}_2$ = molar free energies;
N_1 and N_2 = number of moles of the first and second phases;
σ = interface area.

In accordance with formula $\Phi = F + PV$, we can write a similar formula for the total thermodynamic potential of the two phases

$$\Phi = N_1\mu_1 + N_2\mu_2 + \alpha\sigma. \tag{27.3}$$

If, however, the quantity of the substance in the two adjacent phases is large, the last term in formulae (27.2) and (27.3) is infinitely small and can be ignored, as was done in the preceding discussion. The fact is that the number of moles of the substance in the surface layer is proportional to the area of the interface, i.e. to the linear dimensions squared, while the number of moles in each of the phases is proportional to the volume of the phases, i.e. to the linear dimensions cubed. Thus, the fraction of the substance in the interface is inversely proportional to the linear dimensions and is extremely small for large-size phases.

However, when a substance free of any foreign impurities—dust particles, gas bubbles in a liquid or drops of liquid in a vapour, etc. undergoes a phase transition, the new phase originates in a finely divided form: in the form of small crystals, fine liquid droplets,

vapour bubbles. In these small nuclei of the new phase a considerable proportion of particles is located in the thin surface layer, and the term $\alpha\sigma$ in formula (27.3) becomes significant. This is why the growth of a small enough nucleus of the new phase is disadvantageous from the thermodynamic viewpoint. The fact is that when a substance changes from a phase with a higher chemical potential to a phase with a lower chemical potential, the decrease in the volumetric fraction of the thermodynamic potential would be more than sufficiently compensated for by the increase in the surface energy $\alpha\sigma$ resulting from the increase in the surface area of the nucleus. For this reason the total thermodynamic potential would then increase. It follows from the foregoing that if the nuclei of the new phase are of a fine size, the initial phase is metastable beyond the phase-transition point. In fact, although the total change from the initial phase to the final phase would be accompanied by a decrease in the thermodynamic potential, the initial stage of this transition (the growth of fine nuclei) would require the potential to increase.

Such a situation, naturally, does not arise if there are in the substance sufficiently large centres of formation of a new phase, such as specks of dust and gas bubbles. The relative role of the surface term is then small from the very beginning, and the process of phase transition is not "delayed". It should be noted that for this reason melting and sublimation undergone by a solid are not delayed and there is no region in which superheated crystal exists. This is due to the fact that there always exist on the surface of a crystal crystalline imperfections playing the role of fusion or sublimation centres. It has, however, been shown experimentally that a stable superheated crystal state can be achieved with good monocrystals, if the heating is done from the inside (with the aid, for instance, of a high-frequency field).

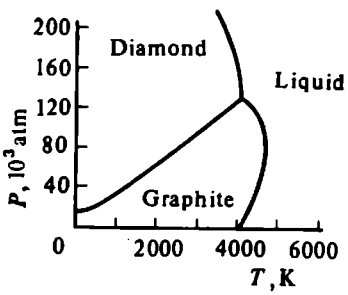


FIG. 46

It is very easy, without taking any special precautions, to arrive at metastable states when different crystal modifications of the same substance undergo phase transitions. This is explained by the fact that the thermal motion of crystal particles takes the form of small oscillations which hamper to a large extent the rearrangement of the crystal lattice. It is clear from Fig. 46, showing the diagram of states of carbon, that diamond can be in a state of thermodynamic equilibrium only at pressures of tens or hundreds of thousands of atmospheres. Meanwhile, diamond is known to exist and be prac-

tically stable at normal pressure as well, meaning that under these conditions diamond is in a metastable state, but its change into a stable phase (graphite) at low temperatures takes an extraordinarily long time. Diamond converts rapidly into graphite when heated in a vacuum (to avoid burning) to temperatures ranging from 1000 to 1200 K.

Let us consider in concluding this section the behaviour of a liquid-phase nucleus in a vapour, depending on its size (see [2]). Assume the drop of liquid to be of spherical shape with a radius r and ignore the effect of the gravity field. We use $\tilde{F}_1$, $\tilde{V}_1$, P_1, N_1 to denote the molar free energy, molar volume, pressure and the number of moles in the drop of liquid, and $\tilde{F}_2$, $\tilde{V}_2$, P_2, N_2 for the same quantities in the vapour; denote by P_0 the external pressure. As was shown in Sec. 24, the criterion for equilibrium at a fixed temperature is that the potential Φ^* attains a minimum value. In this case the chemical potential

$$\Phi^* = U - TS + P_0 V + \alpha\sigma$$
$$= N_1\tilde{F}_1(T, V_1) + N_2\tilde{F}_2(T, V_2) + P_0(N_1\tilde{V}_1 + N_2\tilde{V}_2) + 4\pi r^2\alpha. \quad (27.4)$$

We take the quantities N_1, $\tilde{V}_2$ and r, excluding the fixed temperature, as independent variables of the chemical potential Φ^*. The variables N_2 and $\tilde{V}_1$ are related to N_1 and r by formulae

$$N_2 = N - N_1, \quad \tilde{V}_1 = \frac{4\pi r^3}{3N_1}. \quad (27.5)$$

Find the extremum conditions for the potential Φ^* with respect to $\tilde{V}_2$ and r:

$$\frac{\partial\Phi^*}{\partial\tilde{V}_2} = N_2\left[\frac{\partial\tilde{F}_2}{\partial\tilde{V}_2} + P_0\right] = N_2[-P_2 + P_0] = 0, \quad (27.6)$$

$$\frac{\partial\Phi^*}{\partial r} = N_1\left[\frac{\partial\tilde{F}_1}{\partial\tilde{V}_1} + P_0\right]\frac{4\pi r^2}{N_1} + 8\pi r\alpha = 4\pi r^2\left[-P_1 + P_0 + \frac{2\alpha}{r}\right] = 0. \quad (27.7)$$

It follows from equations (27.6) and (27.7) that $P_2 = P_0$, $P_1 = P_0 + 2\alpha/r$, i.e. in the equilibrium state the vapour pressure is equal to the external pressure, while the pressure in the droplet of the liquid is higher than the vapour pressure by $2\alpha/r$ (pressure at a curved surface). Let us now find the equilibrium criterion with respect to the processes of evaporation and condensation, that is, changes in the number of moles N_1. We have

$$\frac{\partial\Phi^*}{\partial N_1} = \tilde{F}_1(T, V_1) - \tilde{F}_2(T, V_2) + P_0(\tilde{V}_1 - \tilde{V}_2) + N_1\left[\frac{\partial\tilde{F}_1}{\partial\tilde{V}_1} + P_0\right]\frac{\partial\tilde{V}_1}{\partial N_1}$$
$$= (\tilde{F}_1 - \tilde{F}_2) + P_0(\tilde{V}_1 - \tilde{V}_2) - (P_0 - P_1)\frac{4\pi}{3N_1}r^3$$
$$= \mu_1(T, P_1) - \mu_2(T, P_2). \quad (27.8)$$

With a flat interface, the pressure of a saturated vapour is determined by the condition $\mu_1(T, P_{sat}) = \mu_2(T, P_{sat})$. It is clear from (27.8) that at a given pressure $P_2 > P_{sat}$ (the vapour is supersaturated) the droplet will grow when $\mu_1(T_1, P_1) < \mu_2(T_2, P_2)$ and will evaporate when $\mu_1(T_1, P_1) > \mu_2(T_2, P_2)$; the potential Φ^* diminishes in both cases.

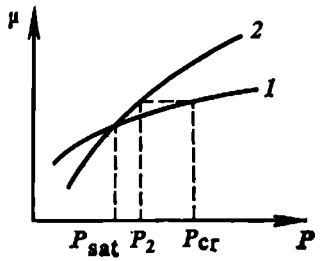


FIG. 47

Figure 47 shows the dependence $\mu(P)$ at $T = \text{const}$ for the liquid (curve *1*) and gaseous (curve *2*) phases. The abscissa of the point of intersection equals the pressure of the saturated vapour. It is clear from the figure that for a drop of liquid to grow the pressure inside the drop must be lower than P_{cr}, determined by formula $\mu_1(T_1, P_{cr}) = \mu_2(T_1, P_2)$. Since $P_{cr} = P_2 + 2\alpha/r_{cr}$, we can determine the radius of the drop

$$r_{cr} = \frac{2\alpha}{P_{cr} - P_2}. \tag{27.9}$$

Drops having a radius $r > r_{cr}$ ($P_2 < P_1 < P_{cr}$) grow; drops with a radius $r < r_{cr}$ ($P_{cr} < P_1$) evaporate. When dealing with slightly supersaturated vapour the chemical potentials μ_1 and μ_2 can be expanded into a series in powers of $(P - P_{sat})$. The equation defining P_{cr} takes on the following appearance:

$$\left(\frac{\partial \mu_1}{\partial P_1}\right)_T (P_{cr} - P_{sat}) = \left(\frac{\partial \mu_2}{\partial P_2}\right)(P_2 - P_{sat}),$$

whence, substituting $\left(\frac{\partial \mu_l}{\partial P_l}\right)_T = \tilde{V}_l$, we obtain, according to Eq. (27.9),

$$r_{cr} = \frac{2\alpha \tilde{V}_1}{(\tilde{V}_2 - \tilde{V}_1)\,\Delta P}, \tag{27.10}$$

where $\Delta P = P_2 - P_{sat}$. The critical radius of a drop is directly proportional to the surface tension and is inversely proportional to the supersaturation ΔP; the more a vapour is supersaturated, the finer are the drops capable of serving as nuclei for the liquid phase.

If a drop carries an electric charge (for instance, a drop originates around an ion), then an additional term appears in the equation for the thermodynamic potential, that is, the free energy of the electric field $\int \frac{\varepsilon E^2}{8\pi} dV$, which is inversely proportional to the drop radius r (see Problem 3 in this section). Inasmuch as this term diminishes as the drop grows, we find a tendency for charged drops to grow even

in an unsaturated vapour. This explains the initiation of showers during thunderstorms, with a large number of ions being formed during electric discharges, and also explains the principle behind the operation of the Wilson cloud chamber.

Problems

1. Find the change in the parameters of the triple point, ΔP_0, ΔT_0, caused by the presence of air in the vessel at a partial pressure P $(P/P_0 \ll 1)$.

Answer. $\dfrac{\Delta P_0}{P_0} = -\dfrac{\tilde{V}_1\lambda_{23}+\tilde{V}_2\lambda_{31}}{\tilde{V}_1\lambda_{23}+\tilde{V}_2\lambda_{31}+\tilde{V}_3\lambda_{12}}$;

$$\frac{\Delta T_0}{T_0} = \frac{P\tilde{V}_3(\tilde{V}_3-\tilde{V}_1)}{\tilde{V}_1\lambda_{23}+\tilde{V}_2\lambda_{31}+\tilde{V}_3\lambda_{12}}$$

(the subscripts 1, 2, 3 pertain to the solid, liquid and gaseous phases respectively; λ_{12}, λ_{23}, λ_{31} are the molar heats of fusion, boiling and crystallization at the triple point; $\lambda_{12} + \lambda_{23} + \lambda_{31} = 0$, λ_{12} and λ_{23} are positive, $\lambda_3 < 0$).

2. A vessel with volume $V = 1.5 \times 10^{-2}$ m^3 contains 0.5 moles of ice $(N_1^{(0)} = 0.5)$, 1 mole of water $(N_2^{(0)} = 1)$ and some number $N_3^{(0)}$ of moles of water vapour. What quantity of heat must be added (removed) for the system to move from the triple point? The molar volumes of ice, water and vapour at the triple point are respectively $\tilde{V}_1 = 19.8 \times \times 10^{-3}$ m^3/kmol; $\tilde{V}_2 = 18 \times 10^{-3}$ m^3/kmol and the molar heats of the phase transition are $\lambda_{12} = 6 \times 10^6$ J/kmol, $\lambda_{23} = 4.5 \times 10^7$ J/kmol, $\lambda_{31} = -5.1 \times 10^7$ J/kmol.

Answer. The triple point can be abandoned in two ways.

1) Along the liquid-vapour equilibrium curve, in which case, at the moment the triple point is left, $N_1 = 0$, $Q_1 = \lambda_{12}(N_2 - - N_2^{(0)}) - \lambda_{31}(N_3 - N_3^{(0)}) \approx \lambda_{12}N_1^{(0)} = 3 \times 10^3$ J.

2) Along the ice-vapour equilibrium curve. In this case $N_2 = 0$, $Q_2 = \lambda_{23}(N_3 - N_3^{(0)}) - \lambda_{12}(N_1 - N_1^{(0)}) \approx -\lambda_{12}N_2^{(0)} = -6 \times \times 10^3$ J. Condensation of all the vapour in the system is impossible.

Hint. The equations defining the number of moles in the system have the form $N_1 + N_2 + N_3 = N_1^{(0)} + N_2^{(0)} + N_3^{(0)}$, $N_1\tilde{V}_1 + + N_2\tilde{V}_2 + N_3\tilde{V}_3 = V$,

$$N_3^{(0)} = \frac{V - N_1^{(0)}\tilde{V}_1 - N_2^{(0)}\tilde{V}_2}{\tilde{V}_3}.$$

3. Consider the conditions for growth of a drop of liquid having radius r at whose centre there is an ion with charge q and

radius a. Answer for unsaturated and supersaturated vapours, depending on r.

Answer. The condition for growth of the drop of liquid is the validity of the inequality $\mu_1(P_1, T) < \mu_2(P_2, T)$, where vapour pressure P_2 is equal to external pressure P_0, and

$$P_1 = P_0 + \frac{2\alpha}{r} - \frac{q^2}{8\pi r^4}\frac{\varepsilon - 1}{\varepsilon},$$

where ε is the dielectric permeability of the liquid. The pressure P_1 is plotted as a function of r in Fig. 48,

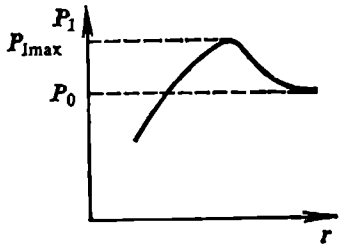


FIG. 48

$$P_{1\max} = \left(\frac{27\pi\alpha^4}{2q^2}\frac{\varepsilon}{\varepsilon - 1}\right)^{1/3} + P_0.$$

In a heavily supersaturated vapour, characterized by the inequality $\mu_1(P_{1\max}, T) > \mu_2(P_0, T)$, all the drops, both of large and small radius, are free to grow. In a slightly supersaturated vapour, characterized by $P_0 > P_{sat}$, $\mu_1(P_{1\max}, T) > \mu_2(P_0, T)$, drops of small radius, $r < r_1$, and large, $r > r_2$, are able to grow, while drops of an intermediate radius are unstable. In an unsaturated vapour only drops of a sufficiently small radius, $r < r_3$, grow. (Estimate r_1, r_2, r_3.)

28. Second-Order Phase Transitions

Along with the first-order phase transitions considered above, during which the chemical potential changes continuously at the transition point, $\mu_1 = \mu_2$, and its first-order derivatives $\left(\frac{\partial\mu}{\partial T}\right)_P = -\widetilde{S}$ and $\left(\frac{\partial\mu}{\partial P}\right)_S = \widetilde{V}$ undergo discontinuity jumps, there also exist phase transitions at which the first-order derivatives of the chemical potential undergo no discontinuity jumps (at the transition point $\widetilde{S}_1 = \widetilde{S}_2$, $\widetilde{V}_1 = \widetilde{V}_2$), and the second-order derivatives

$$\left(\frac{\partial^2\mu}{\partial P^2}\right)_T = \left(\frac{\partial\widetilde{V}}{\partial P}\right)_T, \quad \left(\frac{\partial^2\mu}{\partial T^2}\right)_P = -\frac{C_P}{T}, \quad \frac{\partial^2\mu}{\partial P\,\partial T} = \left(\frac{\partial\widetilde{V}}{\partial T}\right)_P$$

have finite or infinite discontinuities at the phase-transition point. Such phase transitions are said to be continuous. The general theory of continuous phase transitions will be dealt with in Part II of this book (Ch. VIII). This section is confined to a discussion of the so-called *second-order phase transitions*, during which the second-order derivatives of the chemical potential undergo finite discontinuity jumps at the phase-transition point. (Throughout this sec-

tion, we mean by the jumps in thermodynamic quantities finite changes.) Thus, second-order phase transitions do not involve discontinuity jumps in volume, in the absorbtion or liberation of heat of the phase transition, but in such quantities as compressibility, volume expansion coefficient and heat capacity.

Second-order phase transitions are usually associated with abrupt changes in various properties characterizing the symmetry of a body. For instance, if the lattice points of a centered cubic lattice, found at the centres of the cells, experience even the smallest displacements, the lattice symmetry changes abruptly. Another example is the case of a lattice in which atoms of a certain kind can occupy places of two types: their "own" (the probability of which is greater than 1/2) or "foreign" places (the probability of which is less than 1/2).

The two probabilities change with temperature and they become equal at some specific temperature. At that moment the lattice constant diminishes abruptly and, consequently, the lattice symmetry undergoes a discontinuity jump. When a magnetic material changes its state from a ferromagnetic material to a paramagnetic material, the symmetrical arrangement of the elementary magnetic moments undergoes a discontinuity jump.

All these examples show that the discontinuity jumps in symmetry, occurring at the second-order phase transition point, are associated with the displacement of a quite small number of atoms or with their displacement over short distances, the displacement thus causing neither consumption of energy nor a discontinuity jump in volume.

It is not difficult to derive for second-order phase transitions the Ehrenfest equation that replaces the Clausius Clapeyron equation $\frac{dP}{dT} = \frac{\lambda}{T}(V_2 - V_1)$, which clearly can have no application to second-order phase transitions, since the right-hand side of the equation is an indeterminacy of a 0/0 type.

Denote by the symbol $[A] = A_2 - A_1$ the discontinuity jump experienced by the quantity A upon a transition from the first phase to the second and find the increment of the quantity $[\mu]$ upon displacement along the phase-transition curve, accurate in dP and dT to the second-order terms:

$$\Delta[\mu] = \left[\left(\frac{\partial\mu}{\partial P}\right)_T\right] dP + \left[\left(\frac{\partial\mu}{\partial T}\right)_P\right] dT + \frac{1}{2}\left[\left(\frac{\partial^2\mu}{\partial P^2}\right)_T\right](dP)^2 + \left[\frac{\partial^2\mu}{\partial P\,\partial T}\right] dP\,dT + \frac{1}{2}\left[\left(\frac{\partial^2\mu}{\partial T^2}\right)_P\right](dT)^2,$$

or

$$\Delta[\mu] = [\tilde{V}]\,dP - [\tilde{S}]\,dT + \frac{1}{2}\left[\left(\frac{\partial\tilde{V}}{\partial P}\right)_T\right](dP)^2 + \left(\left[\frac{\partial\tilde{V}}{\partial T}\right)_P\right] dP\,dT - \frac{1}{2}\frac{[C_P]}{T}(dT)^2. \quad (28.1)$$

Since for a second-order phase transition $[\tilde{V}] = 0$ and $[\tilde{S}] = 0$, then

$$\Delta[\mu] = \frac{1}{2}\left[\left(\frac{\partial \tilde{V}}{\partial P}\right)_T\right](dP)^2 + \left[\left(\frac{\partial \tilde{V}}{\partial T}\right)_P\right] dP\, dT - \frac{1}{2}\frac{[C_P]}{T}(dT)^2. \quad (28.2)$$

Along the equilibrium phase curve $[\mu] = 0$, and

$$\frac{1}{2}\left[\left(\frac{\partial \tilde{V}}{\partial P}\right)_T\right](dP)^2 + \left[\left(\frac{\partial \tilde{V}}{\partial T}\right)_P\right] dP\, dT - \frac{1}{2}\frac{[C_P]}{T}(dT)^2 = 0. \quad (28.3)$$

Equation (28.3) must provide the differential equation for the equilibrium curve. For the value of $\frac{dP}{dT}$ to be unique, the discriminant of quadratic equation (28.3) must be equal to zero:

$$[C_P]\left[\left(\frac{\partial \tilde{V}}{\partial P}\right)_T\right] + T\left[\left(\frac{\partial \tilde{V}}{\partial T}\right)_P\right]^2 = 0. \quad (28.4)$$

Equation (28.3) can be used to obtain two equivalent expressions for the derivative $\frac{dP}{dT}$ along the phase-equilibrium curve:

$$\frac{dP}{dT} = -\frac{[(\partial \tilde{V}/\partial T)_P]}{[(\partial \tilde{V}/\partial P)_T]}, \quad \frac{dP}{dT} = \frac{[C_P]}{T[(\partial \tilde{V}/\partial T)_P]}. \quad (28.5)$$

The set of equations (28.4), (28.5) is referred to as *Ehrenfest's equations.*

29. Thermodynamics of Superconductors

Many metals and alloys at low temperatures, close to absolute zero, undergo a phase transition passing to the so-called *superconducting state.* The most striking property of substances in this state is the complete absence of resistance to electric current, discovered in the first experimental studies conducted by H. Kamerlingh Onnes in 1911. It should be borne in mind that the current flowing in a conductor is a non-equilibrium process associated with the existence of a flux of charged particles, and, therefore, the effect of vanishing resistance is not a matter for thermodynamics but for kinetics.

The superconducting and normal states of metals, however, happen to differ not only in their conductivities, but also in the magnitudes of a number of purely thermodynamic quantities. This means that these states represent different thermodynamic phases of a substance, with the transition from one state to another being a first-order phase transition if it occurs in a magnetic field, and a second-order phase transition when the magnetic field is switched off.

It should be noted that an analogous situation is encountered in studies of liquid helium. Viscosity, being associated with a non-equilibrium process involving equalization of the velocity of directional motion, is not studied by thermodynamics. However, the superfluid and normal forms of helium (He I and He II) are two thermodynamic phases, and the transition from one phase to the other is a second-order phase transition. For this reason the transition of a metal from the normal to the superconducting state in the absence of current and the transition of He I to He II in the absence of a liquid flow can be studied by thermodynamic methods.

The transition of metal from the normal to the superconducting state is accompanied by a change in its magnetic properties, with the magnetic field failing to penetrate a large superconductor; more precisely, the magnetic field exists only in a thin surface layer about 10^{-5} cm thick. It follows that inside the superconductor

$$\mathbf{B} = 0. \tag{29.1}$$

Since the normal projection of induction, B_n, is continuous on the boundary, the lines of the external magnetic field are tangential to the surface of the superconductor.

In the absence of an applied magnetic field the transition from the normal to the superconducting state occurs at a specific temperature, characteristic of any given superconductor, called the *critical temperature* T_{cr}. In the presence of an applied magnetic field the transition from the normal to the superconducting state or vice versa depends essentially on the shape of the superconductor and can occur at several points of the superconductor simultaneously, if the field is nonuniform along the surface of the metal.

Therefore, we shall limit ourselves to a cylindrical superconductor whose axis is parallel to the applied magnetic field **H**, so that the field is the same at all points on the side surface of the cylinder (not necessarily circular). Superconductivity vanishes in such a cylinder when the intensity of the applied magnetic field reaches a critical magnitude H_{cr}, which depends on temperature, $H_{cr} = H_{cr}(T)$, and becomes zero at $T = T_{cr}$:

$$H_{cr}(T_{cr}) = 0. \tag{29.2}$$

The critical magnetic field intensity H_{cr} is plotted as a function of temperature on the H-T plane, as is shown in Fig. 49. The curve representing the dependence of H_{cr} on T separates the normal n-state from the superconducting s-state. If the cylinder is placed in a field having intensity $H < H_{cr}(0)$, superconductivity sets in at a temperature $T_{cr}(H) < T_{cr}(0)$. The critical temperature T_{cr} introduced above, at which superconductivity vanishes in the absence of an applied magnetic field, is $T_{cr}(0)$. The curve in Fig. 49 is the

locus of the points of phase transition from the n-state to the s-state and vice versa.

If the cylinder is placed in a field with intensity **H**, directed parallel to the cylinder axis, then, as a result of the continuity of the tangential component of the field intensity, the intensity of the field inside the specimen also equals **H**.

By virtue of Eq. (29.1) (it should be recalled that the true averaged field intensity inside a magnetic material is the induction **B**, and not the intensity **H**), we have

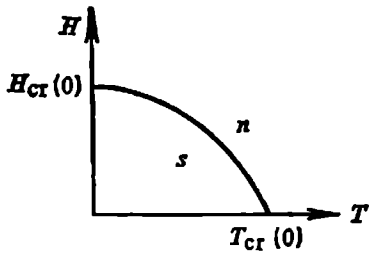


FIG. 49

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} = 0, \quad \mathbf{M} = -\frac{\mathbf{H}}{4\pi}. \tag{29.3}$$

(In this section we use **M** to denote the specific magnetization—the magnetic moment per unit volume.)

It follows from the above that the susceptibility of the superconductor, $\chi_m = \left(\frac{\partial M}{\partial H}\right)_T$, is equal to

$$\chi_m = -\frac{1}{4\pi}. \tag{29.4}$$

Thus, a superconductor can formally be described as an "absolute" diamagnetic material having magnetic susceptibility $\chi_m = -\frac{1}{4\pi}$.

Let us consider a superconductor as a system with two degrees of freedom (generalized coordinates: volume V and total magnetization VM; generalized forces: pressure P and magnetic field H). The thermodynamic potential Φ^* and its differential are then described by

$$\Phi^* = U - TS + PV - HMV, \quad d\Phi^* = -S\,dT + V\,dP - VM\,dH,$$

and the differential of the chemical potential of the superconductor placed in a field is determined by the formula

$$d\mu_s = -\tilde{S}\,dT + \tilde{V}_s\,dP - \tilde{V}_s M\,dH,$$

where $\tilde{V}_s$ = molar volume of the superconductor;
$\tilde{S}$ = molar entropy.

Substitute into the above formula the level of magnetization M from formula (29.3), ignoring the weak effects of magnetostriction such as the dependence of $\tilde{V}$ on H and the dependence of the volume

of the superconductor on external pressure and temperature. Then $\tilde{V}_s = \text{const}$, and we obtain

$$d\mu_s = -\tilde{S}\,dT + \tilde{V}_s\,dP + d\left(\frac{V_s H^2}{8\pi}\right). \tag{29.5}$$

Integrating Eq. (29.5), we find for the superconducting state

$$\mu_s(T, P, H) = \mu_s(T, P, 0) + \frac{\tilde{V}_s H^2}{8\pi}. \tag{29.6}$$

Thus, the chemical potential of a superconductor placed in a magnetic field is greater than that found in the absence of a field by $\frac{\tilde{V}_s H^2}{8\pi}$. On the other hand, the chemical potential of a normal conductor can be assumed to be independent on the magnetic field, since the weak para- and diamagnetism can be ignored in the first approximation. It can, therefore, be taken that

$$\mu_n = \mu_n(T, P). \tag{29.7}$$

Thus, in the presence of a sufficiently strong magnetic field the superconducting state becomes disadvantageous from the thermodynamic viewpoint, $\mu_s(T, P, H) > \mu_n(T, P)$ and superconductivity is destroyed. At the phase-transition points

$$\mu(T, P, 0) + \frac{\tilde{V}_s H_{cr}^2}{8\pi} = \mu_n(T, P). \tag{29.8}$$

Differentiating equation (29.8) with respect to T along the phase-transition curve $H_{cr} = H_{cr}(T)$ and ignoring again the very slight dependence of $\tilde{V}_s$ on T, we obtain

$$\tilde{S}_s - \tilde{S}_n = \frac{\tilde{V}_s H_{cr}}{4\pi}\left(\frac{\partial H_{cr}}{\partial T}\right)_P. \tag{29.9}$$

By analogy, differentiating Eq. (29.8) with respect to pressure, we get

$$\tilde{V}_s - \tilde{V}_n = -\frac{\tilde{V}_s H_{cr}}{4\pi}\left(\frac{\partial H_{cr}}{\partial P}\right)_T. \tag{29.10}$$

Formulae (29.9) and (29.10) show that when the transition from the normal to the superconducting state takes place in a magnetic field at $T < T_{cr}(0)$, it is accompanied by discontinuity jumps in volume and entropy, i.e. a first-order phase transition occurs. Multiplying both sides of Eq. (29.9) by T, we find the expression for the molar heat of a phase transition

$$\lambda = T(\tilde{S}_s - \tilde{S}_n) = \frac{\tilde{V}_s H_{cr} T}{4\pi}\left(\frac{\partial H_{cr}}{\partial T}\right)_P. \tag{29.11}$$

Since $H_{cr}(T)$ is a monotonically decreasing function, $\lambda < 0$. It follows that the transition from the superconductive to the normal

state is accompanied by the absorption of heat and that the reverse transition is accompanied by the liberation of heat.

As to the sign of the difference in volumes, it is determined as can be seen from formula (29.10), by the sign of $\left(\frac{\partial H_{cr}}{\partial P}\right)_T$. This can be both positive and negative for various superconductors, as has been shown experimentally.

Dividing Eq. (29.9) by Eq. (29.10) term-wise, we obtain

$$\frac{\widetilde{S}_s-\widetilde{S}_n}{\widetilde{V}_s-\widetilde{V}_n}=-\left(\frac{\partial H_{cr}}{\partial T}\right)_P\left(\frac{\partial P}{\partial H_{cr}}\right)_T=\left(\frac{\partial P}{\partial T}\right)_{H_{cr}},$$

i.e. the Clapeyron-Clausius equation for the transition from the s-state to the n-state at $H \neq 0$, $T < T_{cr}(0)$:

$$\left(\frac{\partial P}{\partial T}\right)_{H_{cr}}=\frac{\lambda}{T(\widetilde{V}_s-\widetilde{V}_n)}. \qquad (29.12)$$

When the transition from the s-state to the n-state or vice versa is realized at $H = 0$, then $T = T_{cr}(0)$ and $H_{cr} = 0$. The discontinuity jumps in entropy and volume are then equal to zero and the right-hand side of Eq. (29.12) is an indeterminacy of the 0/0 type. In this case the transition from one state to the other is a second-order phase transition.

Let us find the discontinuity jumps in the heat capacity and compressibility in this case. Differentiating Eq. (29.9) with respect to T and multiplying the resulting equation by T, we find, ignoring the dependence of $\widetilde{V}_s$ on T,

$$C_s-C_n=T\left[\left(\frac{\partial \widetilde{S}_s}{\partial T}\right)_P-\left(\frac{\partial \widetilde{S}_n}{\partial T}\right)_P\right]=\frac{\widetilde{V}_s T}{4\pi}\left[H_{cr}\left(\frac{\partial^2 H_{cr}}{\partial T^2}\right)_P+\left(\frac{\partial H_{cr}}{\partial T}\right)_P^2\right]. \qquad (29.13)$$

At $H = 0$, $T = T_{cr}(0)$ and $H_{cr} = 0$ Eq. (29.13) reduces to Rutger's equation

$$C_s-C_n=\frac{V_s T_{cr}}{4\pi}\left(\frac{\partial H_{cr}}{\partial P}\right)_T^2, \qquad (29.14)$$

showing the heat capacity in the superconducting state to be larger than the heat capacity in the normal state.

Differentiating Eq. (29.10) with respect to pressure, we find

$$\left(\frac{\partial V_s}{\partial P}\right)_T-\left(\frac{\partial \widetilde{V}_n}{\partial P}\right)_T=-\frac{\widetilde{V}_s}{4\pi}\left[H_{cr}\left(\frac{\partial^2 H_{cr}}{\partial P^2}\right)_T+\left(\frac{\partial H_{cr}}{\partial P}\right)_T^2\right]. \qquad (29.15)$$

(We do not differentiate the volume V_s on the right-hand side of Eq. (29.10), since this gives only small corrections to Eq. (29.15)

In particular, at $H = 0$

$$\left(\frac{\partial \widetilde{V}_s}{\partial P}\right)_T - \left(\frac{\partial \widetilde{V}_n}{\partial P}\right)_T = -\frac{\widetilde{V}_s}{4\pi}\left(\frac{\partial H_{cr}}{\partial P}\right)_T^2, \qquad (29.16)$$

showing the normal-state compressibility to be smaller than the compressibility in the superconductive state*.

30. Multicomponent Systems. Phase Rule

So far we have considered thermodynamic equilibrium in physically heterogeneous, but chemically homogeneous systems consisting of several phases. Let us turn now to considering systems of complex chemical composition of several components. By *components* of a multicomponent system we mean the chemically different parts of the system, provided that the quantity of each component does not depend on the content of other components.

An example of a two-component (binary) system is a water solution of salt. This is a two-component and single-phase (homogeneous) system. But if the solution is saturated and small salt crystals precipitate from it, it is then a physically heterogeneous system consisting of two phases, but is classified as a two-component system from the chemical viewpoint.

Irrespective of whether water is in the gaseous, liquid or solid states of aggregation, it is a single-component system, since, despite the fact that water consists of hydrogen and oxygen, the amounts of these components are strictly and definitely related. If water undergoes electrolysis, the system becomes a binary one, since the amounts of water and hydrogen (or oxygen) can be preset independently.

Generalizing the conclusions drawn in Sec. 26, we can easily derive the equation of equilibrium for a system consisting of n components and r phases. Surface effects associated with the existence of the surface energy $\alpha\sigma$ will be ignored in this section.

The condition for mechanical equilibrium, fixed interfaces, requires pressure to be the same in all phases, so that we can describe the state of a system in terms of one pressure P. The condition for ther-

* An attentive reader might be puzzled by the fact that in derivin formulae (29.9) and (29.10), $\widetilde{V}_s$ was assumed to be independent of pressure, and when formula (29.15) was derived, $\widetilde{V}_s$ was differentiated with respect to pressure. Formula (29.15) explains this contradiction. It is clear from (29.15) that close to the phase-transition point $\left(\frac{\partial \widetilde{V}_s}{\partial P}\right)$ is small, since the critical field H_{cr} is shown experimentally to depend only slightly on pressure. Therefore, an account of the dependence of H_{cr} on P would lead from the outset to the appearance of terms of a higher order of smallness with respect to $\left(\frac{\partial \widetilde{H}_{cr}}{\partial P}\right)$.

mal equilibrium requires temperature to be the same in all phases, so that a system can be characterized by one temperature T.

Let us now specify the conditions for chemical equilibrium characterized by the requirement that particles do not pass from one phase to another. Considering in Sec. 26 a single-component system, we found as a criterion of chemical equilibrium Eq. (26.3), $\mu_1 = \mu_2$, where $\mu_i = \left(\frac{\partial \Phi}{\partial N_i}\right)$ is the chemical potential of the ith phase. The chemical potential of a multicomponent system depends, in addition to pressure and temperature, on the number of moles of each phase component, and so we can introduce nr chemical potentials $\mu_i^{(k)} = \frac{\partial \Phi_i}{\partial N_i^{(k)}}$, where $N_i^{(k)}$ is the number of moles of the ith component present in the kth phase.

Generalizing Eq. (26.3), we obtain the following relations for chemical equilibrium:

$$\begin{aligned} &\mu_1^{(1)} = \mu_1^{(2)} = \ldots = \mu_1^{(r)}, \\ &\mu_2^{(1)} = \mu_2^{(2)} = \ldots = \mu_2^{(r)}, \\ &\ldots\ldots\ldots\ldots\ldots \\ &\mu_n^{(1)} = \mu_n^{(2)} = \ldots = \mu_n^{(r)}, \end{aligned} \tag{30.1}$$

a total of $n\,(r-1)$ equations. Relations (30.1) can be used to solve practical problems provided the chemical potentials of all phase components of a system are known. However, even without the knowledge of the concrete form of all the chemical potentials $\mu_i^{(k)}$, we can establish the important relation of phase equilibrium, known as the *Gibbs phase rule*.

The state of a multicomponent system for which the masses of all phases are given is characterized by the magnitudes of the intensive parameters T, P and concentrations

$$x^{(k)} = \frac{N_i^{(k)}}{\sum_{i=1}^{n} N_i^{(k)}} \tag{30.2}$$

of the ith component in the kth phase. It should be noted that $x_i^{(k)}$ are interdependent, since for each phase the following relationship is valid:

$$\sum_{i=1}^{n} x^{(k)} = 1. \tag{30.3}$$

Thus, the number of independent concentrations in each phase is equal to $n - 1$. The total number of parameters characterizing the state of a multicomponent system, including T and P, is equal to

$2 + (n - 1) r$. Inasmuch as in a state of thermodynamic equilibrium these parameters obey $n(r - 1)$ equations (30.1), the number of thermodynamic degrees of freedom, i.e. the number of free parameters N that can be changed without disturbing the equilibrium state, is equal to $2 + (n - 1) r - n(r - 1)$, i.e.

$$N = 2 + n - r. \tag{30.4}$$

Since N is non-negative ($N \geqslant 0$) by its very meaning, then

$$r \leqslant n + 2. \tag{30.5}$$

Relations (30.4) and (30.5) represent the statement of the Gibbs phase rule.

For a single-component system $n = 1$, so that

$$N = 3 - r, \quad r \leqslant 3.$$

When $r = 1$, we obtain $N = 2$ and the independently varying parameters are T and P. For $r = 2$, we are on the two-phase equilibrium curve and $N = 1$; this means that of the two variables T and P only one can be given arbitrarily. In fact, the transition temperature on the phase-transition curve is a function of pressure, and vice versa. For instance, when a gas-liquid equilibrium is involved, the pressure of the saturated vapour is a function of temperature, $P_{sat} = f_1(T)$; in the case of coexisting liquid and solid phases the fusion point (temperature) is a function of pressure, $T_{fus} = f_2(P)$. Finally, when $r = 3$, then $N = 0$ and we find ourselves at the triple point, for which the two parameters P_0, T_0 are determined by the equations

$$P_0 = f_1(T_0), \quad T_0 = f_2(P_0). \tag{30.6}$$

It is clear that $r = 4$ is possible in principle (for instance, coexistence of liquid, gaseous and two solid phases), but such coexistence contradicts the Gibbs phase rule.

Let us illustrate once more the Gibbs phase rule, using as an example the binary system, a salt dissolved in water. When $n = 2$, we have

$$N = 4 - r, \quad r \leqslant 4. \tag{30.7}$$

Let $r = 1$ (for instance, a weak solution), then $N = 3$ and all three parameters T, P and x can vary independently, not intersecting the two phase-equilibrium curves.

Let $r = 2$, for instance, with (a) a vapour and a solution; (b) a solution and ice crystals; (c) a solution and salt crystals in equilibrium. Then $N = 2$ and in case (a), for instance, we can preset independently temperature T and concentration x, while the pressure of the saturated vapour is a function only of T and x, as stated by *Raoult's law*, $P_{sat} = f_1(T, x)$. In case (b) we can take independently pressure and concentration, while the fusion temperature is a func

tion of both, $T_{fus} = f_2(P, x)$. In case (c) pressure and temperature can be given independently, while the concentration of the saturated solution is a function of both, $x_{sat} = f_3(P, T)$.

Let $r = 3$, for instance, with (a) a vapour, a solution and salt crystals; (b) a solution, ice crystals and salt crystals; (c) a vapour, a solution and ice crystals in equilibrium. Then, $N = 1$. In case (a), for instance, we can assume an arbitrary temperature, with the pressure of the saturated vapour and the concentration of the saturated solution being determined by the equations

$$P_{sat} = f_1(T, x_{sat}), \quad x_{sat} = f_3(P_{sat}, T).$$

In case (b) we can set pressure, with the fusion point and concentration of the saturated solution being determined by the equations

$$T_{fus} = f_2(P, x_{sat}), \quad x_{sat} = f_3(P, T_{fus}).$$

In case (c) concentration can be set at will, while the pressure of the saturated vapour and the fusion point are determined by the equations

$$P_{sat} = f_1(T_{fus}, x), \quad T_{fus} = f_2(P_{sat}, x).$$

Let, finally, $r = 4$ (for instance, a vapour, a solution and crystals of ice and salt are in equilibrium). Then, $N = 0$. Such equilibrium is possible only at fixed values of all the parameters P_0, T_0, x_0, which are determined by the equations

$$P_0 = f_1(T_0, x_0), \quad T_0 = f_2(P_0, x_0), \quad x_0 = f_3(P_0, T_0).$$

It is clear that the equilibrium coexistence of five phases, for instance, of a vapour, a solution, salt crystals and two crystal modifications of ice, though possible in principle, is ruled out by the Gibbs phase rule.

Problem

Consider an aqueous solution of two different substances not reacting with each other. Determine the number of thermodynamic degrees of freedom for a different number of coexisting phases. What is the maximum number of coexisting phases?

31. Chemical Equilibrium in a Homogeneous System. The Mass Action Law

Let a chemical reaction occur in a homogeneous thermodynamic system, that can be described by

$$\sum_i \nu_i A_i = 0, \tag{31.1}$$

where A_i = chemical symbols of the reacting substances;
ν_i = stoichiometric coefficients indicating how many molecules of the ith substance appear ($\nu_i > 0$) or disappear ($\nu_i < 0$) as a result of a single act of reaction.

For instance, for the ammonia formation reaction

$$2NH_3 - 3H_2 - N_2 = 0$$

we have

$$\nu_1 = \nu(NH_3) = 2,\ \nu_2 = \nu(H_2) = -3,\ \nu_3 = \nu(N_2) = -1.$$

Along with the direct chemical reaction, a reverse chemical reaction can also occur in the system, with one of the reactions prevailing over the other until equilibrium sets in. In the state of thermodynamic equilibrium the direct and reverse reactions balance each other, and the concentrations of the initial and final reaction products remain constant.

Let a reaction proceed at constant pressure and temperature. Thermodynamic equilibrium sets in when the thermodynamic potential assumes a minimum value,

$$d\Phi = -S\,dT + V\,dP + \sum_i \mu_i\,dN_i = 0,$$

and by virtue of the conditions $T = \text{const}$, $P = \text{const}$,

$$\sum_i \mu_i\,dN_i = 0. \tag{31.2}$$

But $dN_i = \nu_i z/N_A$, where z is the number of reaction acts and N_A is Avogadro's number; whence we find the condition of chemical equilibrium,

$$\sum_i \mu_i \nu_i = 0, \tag{31.3}$$

derived from the reaction equation (31 1), replacing the chemical symbols A_i in it with the relevant chemical potentials μ_i. If several chemical reactions occur in a system, then the state of equilibrium is determined by a number of equations of the type (31.3). To solve practical problems with the aid of Eq. (31.3), we must have at our disposal the expressions of the chemical potentials of all substances involved in the system.

Let us consider the conditions of chemical equilibrium for a mixture of perfect gases. The chemical potentials of a mixture of perfect gases can be readily found by means of relationships

$$\Phi = U - TS + PV,\quad U = \sum_i N_i (C_{V_i} T + q_i),$$
$$S = \sum_i N_i [C_{P_i} \ln T - R \ln P_i + S_{0i}],\quad PV = \sum_i N_i RT, \tag{31.4}$$

where P_i = partial pressure of the ith gas; $P_i = PN_i/\sum N_i = Px_i$;
x_i = concentration of the ith gas;
q_i = internal energy of a mole of a gas at $T=0$ (the chemical energy, including the molecular and atomic binding energy);
S_{0i} = entropy constant.

Equations (31.4) are used to find

$$\mu_i = \frac{\partial \Phi}{\partial N_i} = C_{P_i}T + q_i - C_{P_i}T \ln T - S_{0i}T + RT \ln P_i = \\ = RT \ln P_i + \chi_i(T), \tag{31.5}$$

where the quantity

$$\chi_i(T) = q_i + C_{P_i}T(1 - \ln T) - S_{0i}T \tag{31.6}$$

will be referred to as the *chemical constant* of the ith gas. Substituting Eq. (31.5) into Eq. (31.3), we obtain

$$\sum_i \nu_i [RT \ln (x_i P) - \chi_i(T)] = 0,$$

whence

$$\sum_i \nu_i \ln x_i = -\ln P \sum_i \nu_i - \frac{\sum \nu_i \chi_i(T)}{RT}$$

and

$$\prod_i x_i^{\nu_i} = K(P, T), \tag{31.7}$$

where the quantity $K(P, T)$, the *reaction constant*, is determined by the formula

$$K(P, T) = P^{-\sum_i \nu_i} \exp\left[-\sum_i \frac{\nu_i \chi_i(T)}{RT}\right] \tag{31.8}$$

and depends on pressure, temperature and the reaction involved. Formula (31.8) expresses the *law of mass action*. The left-hand side of this formula is actually a fraction with a numerator representing the concentrations of appearing substances and a denominator the concentrations of disappearing substances. Therefore, the greater the reaction constant $K(P, T)$, the greater the shift of the equilibrium in the direction of the reaction end products, and vice versa.

In this connection it is important to know the dependence of K on pressure and temperature. As to the dependence on pressure, it is determined by the factor $P^{-\sum_i \nu_i}$, and, depending on the magnitude of $\sum \nu_i$, three cases may be singled out.

1. $\sum \nu_i > 0$. The reaction results in the number of molecules (and, consequently, the gas volume) increasing. An increase in pressure leads to a smaller reaction constant and, consequently, to a smaller yield of reaction end products.

2. $\sum \nu_i < 0$. The number of molecules (and the gas volume) diminish in the course of the reaction. An increase in pressure is accompanied by an increase in the reaction constant and in the yield of reaction end products.

3. $\sum \nu_i = 0$. The number of molecules (and gas volume) do not change in the reaction. The reaction constant and the yield of reaction end products are independent of pressure.

To elucidate the nature of the dependence of $K(P, T)$ on temperature, let us calculate

$$\frac{\partial}{\partial T}[\ln K(P, T)] = \frac{\sum_i \nu_i [\chi_i(T) - T\chi_i'(T)]}{RT^2}.$$

Substituting the value of $\chi_i(T)$ from formula (31.6), we find

$$\frac{\partial}{\partial T}[\ln K(P, T)] = \frac{\sum_i \nu_i (C_{V_i} T + q_i) + \sum_i \nu_i RT}{RT^2} = \frac{\sum_i \nu_i [C_{V_i} T + q_i] + P \sum_i \nu_i V}{RT^2},$$

where V is the volume of one mole of a gas. It is clear that the first term in the numerator of the right-hand side of the above equation represents the change in the internal energy of the gas mixture, and the second term is the work done in the reaction, both terms pertaining to N_A reaction acts. Therefore,

$$\frac{\partial}{\partial T}[\ln K(P, T)] = \frac{Q}{RT^2},$$

where Q is the heat liberated or absorbed during the reaction per N_A reaction acts.

Hence, at $Q > 0$ (endothermic reaction) we have

$$\frac{\partial}{\partial T}[\ln K(P, T)] > 0.$$

With rising temperature the reaction constant and, consequently, the yield of reaction end products increase.

On the contrary, at $Q < 0$ (exothermic reaction) we have

$$\frac{\partial}{\partial T}[\ln K(P, T)] < 0.$$

The reaction constant and the yield of reaction end products diminish with rising temperature.

Turning from a purely phenomenological discussion, it is wise to note the following obvious molecular-kinetic meaning of the mass action law. Rewrite the reaction equation (31.1) to read

$$\sum_k |\nu_k| A_k \rightleftarrows \sum_i \nu_i A_i,$$

where the subscript i pertains to the conditionally "appearing" substances, and the subscript k to the conditionally "disappearing" substances. In this form the equivalency of the direct and reverse reactions becomes obvious. For one act of the direct reaction to occur within the range of action of chemical forces, ν_i molecules (atoms, ions) of the ith substance must draw together ("collide"). The probability of this act and, consequently, the probability of the direct reaction $w_{\rightarrow}$ are proportional to the partial pressure of the ith gas raised to the ν_i power:

$$w_{\rightarrow} = A(T) P^{\sum_i \nu_i} \prod_i x_i^{\nu_i}. \tag{31.9}$$

For one act of the reverse reaction to occur, $|\nu_k|$ molecules of the kth substance must draw together, and

$$w_{\leftarrow} = B(T) P^{\sum_k |\nu_k|} \prod_k x_k^{|\nu_k|}. \tag{31.10}$$

In formulae (31.9) and (31.10) $A(T)$ and $B(T)$ are factors depending on the "mechanism" of the direct and reverse reactions and on the mean kinetic energy of molecules, i.e. on T. In a state of dynamic equilibrium $w_{\rightarrow} = w_{\leftarrow}$ and we come to the relationship

$$\frac{\prod_i x_i^{|\nu_i|}}{\prod_k x_k^{|\nu_k|}} = P^{\sum_k |\nu_k| - \sum_i \nu_i} \frac{B(T)}{A(T)} = K(P, T), \tag{31.11}$$

which is another mathematical statement of the mass action law, described above by Eqs. (31.7), (31.8).

The derivation of these formulae within the scope of thermodynamics makes it possible to consider in greater detail the dependence of the reaction constant on temperature, and the advantage of the elementary derivation based on kinetics lies in the greater ease of its physical visualization. We shall consider again the mass action law within the framework of statistical physics in Sections 49 and 50, where we shall examine two physical problems—the ionization of atoms and the dissociation of molecules of a diatomic gas.

We shall limit ourselves in this section to the consideration of a purely chemical example.

Consider the reaction of dissociation of hydrogen iodide:

$$H_2 + I_2 - 2HI = 0$$

$$\nu(H_2) = 1, \quad \nu(I_2) = 1, \quad \nu(HI) = -2. \tag{31.12}$$

Assume a vessel to contain initially N_1 moles of non-dissociated HI and N_2 moles of H_2. Denoting the degree of dissociation by $\alpha = \frac{N_1 - N(HI)}{N_1}$, for the number of moles of H_2, I_2, HI we obtain

$$N(H_2) = N_2 + \frac{1}{2}\alpha N_1, \quad N(I_2) = \frac{1}{2}\alpha N_1, \quad N(HI) = N_1(1-\alpha)$$

and the equation describing the mass action law acquires the form

$$\frac{1}{4}\frac{\alpha[\alpha + (2N_2/N_1)]}{(1-\alpha)^2} = K(T). \tag{31.13}$$

The reaction constant is independent of pressure ($\sum_i \nu_i = 0$) and increases rapidly with temperature—the reaction (31.12) is an endothermic one. At low temperatures $K(T) \ll 1$ and $\alpha \ll 1$. Then, the root of Eq. (31.13) approximately equals $\alpha = -\frac{N_2}{N_1} + \sqrt{\left(\frac{N_2}{N_1}\right)^2 + 4K}$; the degree of dissociation $\alpha = 2\sqrt{K}$ in the absence of excessive hydrogen ($N_2 = 0$) and $\alpha \approx 2K(N_1/N_2)$ at $N_2/N_1 \gg K$.

At high temperatures $K(T) \gg 1$ and the degree of dissociation is also close to unity. Replacing in the numerator $\alpha \approx 1$, we obtain

$$1 - \alpha = \left(\frac{1 + 2\frac{N_2}{N_1}}{4K}\right)^{1/2} \quad \text{or} \quad \alpha = 1 - \frac{1}{2}K^{-1/2} \quad \text{at} \quad N_2 = 0$$

and

$$\alpha = 1 - \left(\frac{N_2}{2N_1K}\right)^{1/2} \quad \text{at} \quad \frac{N_2}{N_1} \gg 1.$$

Thus, an excessive amount of one of the components decreases the degree of dissociation. The physical meaning of this conclusion is obvious—an excessive amount of H_2 or I_2 raises the probability of the reverse process in which atoms of H_2 and of I_2 combine into a molecule.

Problem

What proportion of the initial numbers of moles of H_2 and N_2 will ensure a maximum yield of ammonia in the reaction $2NH_3 - N_2 - 3H_2 = 0$, if $P = \text{const}$, $T = \text{const}$?

Answer. $y = \frac{x_{H_2}}{x_{N_2}} = 3$.

Hint. For the given reaction the mass action law provides the equation

$$\frac{x_{NH_3}^2 (1+y)^4}{y^3 (1-x_{NH_3})^4} = K,$$

determining x_{NH_3} as an implicit function of y.

PART TWO

STATISTICAL PHYSICS

CHAPTER III

STATISTICAL DISTRIBUTIONS FOR IDEAL GASES

32. Statistical Regularities. Distributions, Most Probable Distributions

As has already been stated in Introduction, the main objective of statistical physics can be formulated as follows: knowing the laws governing the motion of individual particles of a system, to establish the behaviourial laws for macroscopic quantities of a substance. For this reason statistical physics offers a theoretical substantiation of thermodynamic laws on the basis of atomic and molecular ideas.

This, however, does not exhaust the content of statistical physics. Thermodynamic methods are of no help in deriving an equation of state for a thermodynamic system, that would enable the equations of thermodynamics to be given a concrete physical content, or more exactly to find any thermodynamic function. In contrast to thermodynamics, the statistical method permits one in principle to find the equation of state of any thermodynamic system. However, due to various difficulties, mainly mathematical, this problem cannot thus far be fully solved for a number of real systems.

In order to gain some insight into the essence of statistical methods, let us consider by way of example a gas consisting of a large number N of molecules. We will deliberately use Newton's classical mechanics to describe the state of the gas in this and in the following section, and only later will we make use of a quantum-mechanical description. The purpose of doing so will become clearer below (Sec. 52): we intend to show that many ideas of wave mechanics are deeply rooted even in classical statistical physics and that the possibility was already there, on the basis of the previously elaborated statistical methods of describing ideal gases, for the appearance in physics of the quantum-

mechanical constant h, Planck's constant, long before Planck and Einstein published their papers.

Ignoring the intramolecular structure a gas can be visualized as a system of N interacting particles, moving in a way prescribed by the laws of Newtonian mechanics. The equation of motion can readily be written down for each of the N molecules

$$m_i \frac{d\mathbf{v}_i}{dt} = \sum_{i \neq k} \mathbf{F}_{ik}, \tag{32.1}$$

where $\mathbf{v}_i$ = velocity of the ith molecule;

$\mathbf{F}_{ik}$ = force of interaction of the ith and kth molecules.

To integrate this system, we must firstly know the force of molecular interaction or the interaction potential as a function of molecular spacing, providing a problem which cannot by any means be fully solved by atomic (nuclear) physics methods. Secondly, we must know $6N$ initial conditions—initial coordinates x_i, y_i, z_i and the projections of the initial velocity v_{xi}, v_{yi}, v_{zi} for each molecule. But even if we had such information, it would be practically impossible to integrate Eq. (32.1) and find the path and law of motion for each molecule, on account of the great number of equations (it should be recalled that under standard conditions 1 m^3 of a gas contains 2.7×10^{25} molecules). It should also be noted that even if it were possible, integration of system of equations (32.1) would be a fruitless expenditure of time, since the knowledge of the paths and laws governing the motion of individual molecules offers no information on the properties of a gas as a whole. Here a new circumstance must be considered: in a system consisting of a great number of particles new purely statistical or probability laws take effect that are foreign to a system containing a small number of particles.

To understand the essence of these new laws, let us consider the following ideal situation: assume it is possible to measure rapidly and with great accuracy the energy of each molecule of a gas. The results of such measurement are presented graphically in Fig. 50 (energy histogram) plotted in the following way. The axis of the abscissae on which the energy is laid off is subdivided into equal sections each ε_0 long. The selection of ε_0 is arbitrary over a wide range and is dictated only by convenience (it will be seen below that it is convenient to select ε_0 sufficiently small that in the interval $l\varepsilon_0$, $(l + 1)\varepsilon_0$ all energies can be assumed to be almost the same and equal to $\varepsilon_l \approx l\varepsilon_0$).

Further, we find the relative number of molecules with energies in the range $l\varepsilon_0$, $(l + 1)\ \varepsilon_0$. Denoting the number of molecules by $n(l)$, let us introduce the definition

$$n(l) = \frac{N(l, l+1)}{N}, \tag{32.2}$$

where $N(l, l+1)$ = the number of molecules with energies in the range that is of interest to us;
N = the total number of molecules.

The function $n(l)$ will be referred to as the *energy distribution function for molecules*, or simply the *energy distribution*. Plotting the values of $n(l)$ on the y-axis, we obtain the system of rectangles depicted in Fig. 50.

When plotting an actual histogram, as well as subdividing the x-axis into equal segments ε_0, it is also convenient (for reasons that will be elucidated in Sec. 33 we shall refer to them as *cells*) to divide the x-axis into longer unequal segments that will be called *boxes* (Sec. 33). This is explained by the fact that the number of molecules with either very low energies or very high energies is very small,

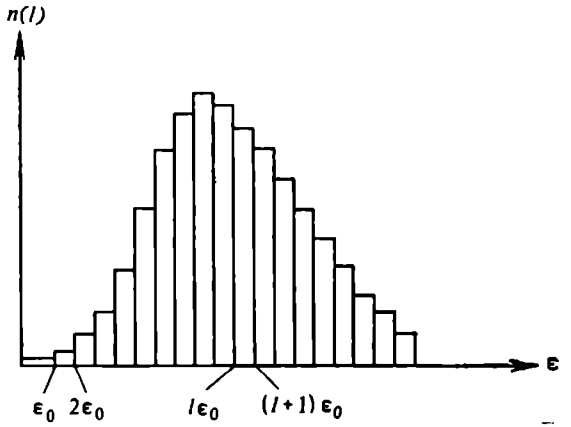


FIG. 50

and the number varies strongly from one experiment to the other. It is therefore convenient to combine in these regions several cells (m, for instance) into a larger unit, a box. The relative number of molecules with energies in the range $l\varepsilon_0$ to $(l+m)\varepsilon_0$, where $m\varepsilon_0$ is the length of a box, is more stable and varies little from experiment to experiment. For the histogram not to distort the distribution pattern, the relative number of molecules with energies ranging from $l\varepsilon_0$ to $(l+m)\varepsilon_0$ must, of course, be divided by m, i.e. be referred to one cell, and the result must be plotted on the coordinate axis. Repeating this experiment with the same gas in an equilibrium state and at the same temperature and pressure, we plot histograms differing only slightly from one another. All the histograms will be close to some averaged histogram and large deviations from it will be rare, the reason for this being as follows. From the viewpoint of

classical mechanics, to describe the state of a gas at some moment of time means to give the coordinates x_i, y_i, z_i and the velocity projections v_{xi}, v_{yi}, v_{zi} of all molecules of the gas. Such a detailed description implies that the *microstate* of the gas is given. For each energy distribution of gas particle there exists a great number of microstates, since at a fixed energy a particle may have different coordinates and different velocity projections satisfying the condition

$$\frac{m_i(v_{xi}^2+v_{yi}^2+v_{zi}^2)}{2}+\mathcal{U}(x_i, y_i, z_i)=\varepsilon,$$

where the term $\mathcal{U}(x_i, y_i, z_i)$ is the potential energy of a molecule. For some energy distributions there exist great numbers of microstates, but for other distributions—lesser numbers. There exists an energy distribution for molecules that is realized with a maximum number of microstates, this maximum being quite high for macroscopic masses of gas (for further details, see Sec. 61). This means that such a distribution, referred to below as the *most probable*, is the most commonly realized and that the gas is evidently in a state with such an energy distribution for almost the whole period of time. This ideal experiment yields with overwhelming probability histograms which must be close to that corresponding to the most probable distribution.

All the above pertains, of course, not only to energy distribution of particles, but also to distributions of other physical quantities. We could study, for instance, coordinate, momentum and angular momentum distribution of gas molecules.

Let us turn now to the thermodynamic description of the state of a gas, recalling that in thermodynamics the state of a gas is described in terms of such macroscopic parameters as pressure, temperature, etc. Let us consider it from the viewpoint of statistical physics. Gas pressure, for instance, is defined as the average force with which gas molecules strike 1 cm^2 of the wall of a confining vessel, $P=\overline{f}/\sigma$ (here and below the mean value of a quantity will be identified by a bar above its symbol).

The well-known elementary formula for the mean kinetic energy of the translational motion of a gas molecule,

$$\frac{m\overline{v^2}}{2}=\frac{3}{2}kT, \tag{32.3}$$

shows the absolute temperature T to be a measure of the mean kinetic energy of the gas molecule. It is also natural to identify the thermodynamic internal energy of a system, U, with the mean energy of molecules or atoms, ions, etc. of the system.

The examples considered above show the macroscopic parameters P, T, U, etc. to represent the mean values of quantities pertaining to individual molecules. It is one of the main objectives of statistical

physics to find such mean values and elucidate the relations between them.

Let us pose the question what information on gas molecules is needed in order to find, for instance, the mean energy of a molecule. It is clear that this information must include the energy distribution of molecules.

In fact, knowing the function $n(l)$, we find

$$\bar{\varepsilon} = \sum_l \frac{N(l, l+1)\,\varepsilon_l}{N} = \sum_l n(l)\,\varepsilon_l \qquad (32.4)$$

(energy ε_0 is assumed to be small compared with ε_l, so that the change in energy along the length of a cell is immaterial). In a similar way it is possible to find the mean values of any energy functions, and any functions of coordinates and momenta, if the coordinate distribution or the momentum distribution are known.

Thus, it is clear that in addition to the description of a macroscopic system by methods of phenomenological thermodynamics, another description is possible, based on an atomic and molecular model and probabilistic ideas, that is, a statistical description. The two methods are related by the *basic physical postulate of statistical physics*, according to which the distribution realized by the greatest number of microstates is the most probable distribution and is equivalent to the equilibrium state of thermodynamics.

Let us point out here the fundamental difference between the thermodynamic and statistical interpretations of the concept of the equilibrium state. Phenomenological thermodynamics assumes that in the absence of external effects a system remains in a state of equilibrium indefinitely long. From the viewpoint of statistical physics the system remains in that state for almost the whole period of time. In this connection statistical physics predicts the existence of *fluctuations* (discussed in detail in Ch. VII), i.e. of spontaneous and extremely rare deviations from the equilibrium state in macroscopic bodies. This means a violation of the laws of phenomenological thermodynamics.

Thus, the most important problem of statistical physics is finding distributions with the highest probabilities. It should be stressed once more that the findings of statistical thermodynamics are only valid for systems with a very large number of particles. The smaller the number of particles in a system, the more often distributions are encountered differing markedly from the most probable. This means that a system with a small number of particles is in the most probable (equilibrium) macroscopic state and in other (non-equilibrium) states over intervals of time of the same order of magnitude. For this reason the use of most probable distributions becomes unjustified.

Hence statistical thermodynamics is an *asymptotic theory* whose findings (except for the theory of fluctuations) are precisely valid

within the limits $N \to \infty$ and $V \to \infty$ (with the ratio N/V remaining constant). Such a limiting transition is known as the *thermodynamic transition* to the limit. In the formulae of statistical thermodynamics terms including high powers of N^{-1} should be ignored, only terms with the lowest power of N^{-1} being retained. Turning to the problem of finding the most probable distribution, we shall consider in this section the simplest part of this problem, i.e. the finding of the most probable distributions for ensembles of non-interacting particles, or for ideal gases.

The statistical properties of ideal gases can be studied by means of a rather general, but at the same time sufficiently simple method—the box and cell method. In spite of the fact that an ideal gas is a particular case, it does cover a great number of real physical problems which can be solved completely.

33. μ-Space. Boxes and Cells

To find statistical distributions the concept of the phase μ-space must be introduced. In the simplest case of a monoatomic ideal gas, gas molecules (atoms) are assumed to be material points, their internal structure being neglected. By the μ-space we mean a six-dimensional space, the coordinates of which are the three spatial coordinates of a molecule, x, y, z, and three momentum projections, ξ, η, ζ. The state of each gas molecule is represented in the μ-space (from the viewpoint of classical physics) by a point, and the state of the entire gas by the totality of N points (N is the total number of molecules). The molecular coordinates and momenta vary with time, and the representative points in the phase space move along certain trajectories. During the time between two collisions the phase trajectory of each molecule lies on the constant-energy hypersurface. This five-dimensional surface is specified by the equation

$$\varepsilon = \frac{\xi^2+\eta^2+\zeta^2}{2m} + \mathcal{U}(x, y, z). \tag{33.1}$$

By analogy with the usual three-dimensional space, the concept of the phase volume in the μ-space is introduced. By an element of volume we mean the expression

$$d\Gamma = dx\, dy\, dz\, d\xi\, d\eta\, d\zeta, \tag{33.2}$$

that is subdivided into the products of the volume elements in the configurational space

$$dV = dx\, dy\, dz$$

and in the momentum space

$$dV_p = d\xi\, d\eta\, d\zeta.$$

Depending on the symmetry of the problem, it might be convenient to select as volume elements both in the configurational and momentum spaces not the Cartesian rectangular parallelepipeds but, for instance, the spherical layers: $dV = 4\pi r^2\, dr$ and $dV_p = 4\pi p^2\, dp$, etc.

The simplest graphical model of the μ-space is the μ-plane for unidimensional motion (Fig. 51).

Let us consider by way of the simplest example a unidimensional "gas" placed in a gravitational field. The constant-energy lines are determined by the equation

$$\varepsilon = \frac{\xi^2}{2m} + mgx$$

and are parabolas with OX as an axis, with the elements of phase volume being represented by area elements $dx\, d\xi$. A collision of two molecules results simply in that their representative points pass from one parabola to another, the total energy being conserved. The concept of the μ-space can readily be extended to cover more intricate systems than a monoatomic gas.

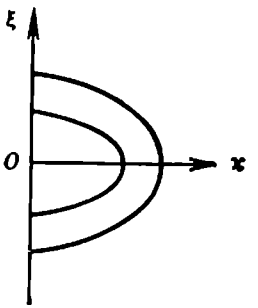


FIG. 51

Let us assume an ideal gas consisting of molecules, each having f degrees of freedom (for instance, for a diatomic gas $f = 6$, for a triatomic gas $f = 9$). The μ-space will then have not 6 but $2f$ dimensions and its coordinates will be f generalized coordinates q_i and f generalized momenta p_i ($i = 1, 2, \ldots, f$). These generalized coordinates are chosen, as is usual in mechanics, in accordance with the symmetry of the problem, while the generalized momenta are defined as the derivatives of the Lagrangian $p_i = \frac{\partial L}{\partial \dot{q}_i}$.

The energy of the gas can be represented by the expression

$$\varepsilon = \sum_{i,k} a_{ik}(q_l)\, p_i p_k + \mathcal{U}(q_l), \tag{33.3}$$

where $\sum_{i,k} a_{ik} p_i p_k$ = kinetic energy of the gas, which is homogeneous quadratic function;

$\mathcal{U}(q_l)$ = potential energy.

Equation $\varepsilon = \text{const}$ is the equation of a constant-energy hypersurface of $2f - 1$ dimensions. The phase μ-volume is specified, as before,

by

$$d\Gamma = dV\, dV_p = \prod_{i=1}^{f} dq_i\, dp_i.$$

The points representing the state of a molecule in an equilibrium state fill the μ-space with some density ρ, that depends in a specific way on q_i, p_i but is independent of time. This means that some ranges of values of coordinates and momenta of system particles are more probable than others and, consequently, that some regions of the phase space are filled by the representative points at a higher density, and others at a lower density.

Let us try to find the most probable distribution of the representative points in the μ-space. This distribution will be described by a certain function of coordinates and momentum projections $\rho(q_i, p_i) = \frac{dN}{d\Gamma}$, where dN is the number of representative points present in an element of phase volume $d\Gamma$. The function $\rho\ (q_i,\ p_i)$ allows us to determine the most probable distribution of molecules both in an ordinary space (coordinate distribution), for which purpose the function $\rho\ (q_i,\ p_i)$ must be integrated over the momenta; and in the momentum space (momentum distribution), for which purpose the function $\rho\ (q_i,\ p_i)$ must be integrated over the coordinates. In accordance with what was stated in Sec. 32, this distribution permits a comprehensive statistical description of gas properties.

Let us introduce now the following important postulate: the distribution function for the μ-space, $\rho\ (q_i,\ p_i)$, depends only on the particle energy $\varepsilon = \sum_{i,\ k} a_{ik} p_i p_k + \mathcal{U}(q_i)$ and not on q_i and p_i individually. (The validity of this postulate will be demonstrated in Sec. 60, in which an important Liouville's theorem will be proved.)

The statistical description of a gas will be undertaken in the same way as when studying the energy distribution of molecules, introducing the subdivision of the μ-space into "boxes" and "cells". Since, in accordance with the postulate the distribution function depends only on energy, we subdivide the space into boxes, carefully drawing the hypersurfaces of constant energy. On the one hand, the energy layers (boxes) used to dissect the μ-space must be sufficiently thin that the representative points confined within the layer can reasonably be given the same energy ε. On the other hand, the layers must be big enough that the number of representative points in the layer N_i is greater than unity, $N_i \gg 1$.

The feasibility of taking a layer of such a thickness will bo discussed in Sec. 39. For the present we shall simply note that by virtue of these restrictions the energy boxes in general will not be equidimensional, since the layers associated with very high or very low energies must be selected so as to be "thicker" than the layers represent-

ing moderate energies, so as to contain a sufficiently large number of representative points.

The second element required for the statistical description are equidimensional cells. These cells must be introduced because the occupation numbers must pertain to equidimensional cells, not non-equidimensional boxes, for all the states to be interpreted in the same manner.

Thus, we introduce the subdivision of the μ-space into equidimensional cells possessing a phase volume a. The shape of the cells is not fixed, although they must not be elongated excessively in any directions. As regards the magnitude of the cell volume a, the situation encountered here differs drastically from that we met in the case of determining the size of the energy layers. The size of the boxes was determined according to the requirements $N_i \gg 1$ and $\varepsilon_{l+1} - \varepsilon_l \ll \varepsilon_l$ only by the order of magnitude, the sizes not being fixed exactly. The volume of a cell a is determined unambiguously by the laws of nature in an amazing manner, as will be described below It should be noted that the volume of a cell is likely to be rather small and, therefore, the energy boxes contain not only a great number of particles ($N_l \gg 1$), but also a large number of cells, $g_l \gg 1$.

Problems

1. On the μ-plane of a one-dimensional gas placed in a gravitational field the representative points occupy the rectangle ξ, $\xi + d\xi$, x, $x + dx$. How will the form and phase volume (area) of these states change in the time Δt as a consequence of the classical equation of motion?
2. The same for a one-dimensional oscillator $\varepsilon = \frac{\xi^2}{2m} + \frac{\varkappa x^2}{2}$.

34. Bose-Einstein and Fermi-Dirac Distributions

We introduced in the preceding section the subdivision of the μ-space into non-equidimensional energy boxes and equidimensional cells. Let the ith energy cell, having an energy ε_i, contain g_i cells and N_i representative points (particles). Of interest is the number of different methods that can be used to realize such a distribution of representative points among the cells*. By virtue of equivalence of cells we consider any arrangement of representative points in the cells to be *equiprobable* and, therefore, the distribution that is re-

* This problem is equivalent to the following combinatorial problem. Assume a number of boxes, of which the ith box is subdivided into g_i cells and contains N_i balls. By what number of methods can such a distribution be realized? This analogy provides an understanding of the origin of the terms "boxes" and "cells".

alized by the greatest number of methods will be assumed to be the most probable distribution, corresponding to the equilibrium state of the gas.

The solution of the combinatorial problem depends to a great extent on certain properties of the system particles. First of all, two different hypotheses can be suggested a priori concerning the system particles (electrons, photons, atoms, ions, etc.): (1) all particles of one kind are absolutely identical to one another, (2) these particles differ slightly in such parameters as mass, charge, etc. (having in mind only constant parameters, and not variable ones such as velocity, energy, etc.), just as production-line identical parts produced in a factory differ from one another. Clearly it is impossible to choose between the two hypotheses by measuring corresponding parameters, due to the existence of inevitable measurement errors and the great number of particles. It will be shown, however, that theoretical arguments permit the problem to be solved uniquely in favour of the hypothesis according to which particles of one kind are identical.

Having assumed the validity of this hypothesis, we may nevertheless consider these identical particles to be distinguishable from each other. This means that each particle of a system can be assigned a number (mentally we can label each particle with a number) and that we can later trace the motion of each particle and distinguish it from the remaining particles. The state of the system in which the coordinates and momenta of the ith particle are q_i and p_i and of the kth particle q_k and p_k, and the state in which the ith and kth particles change places in the μ-space, can then be considered as different states.

The hypothesis according to which identical particles are indistinguishable from each other and the states of a system differing only in the rearrangement of particles are the same states is, however, more probable. In this section we shall be guided by this hypothesis, and the corollaries of the hypothesis on the ability to distinguish identical particles will be treated in Sec. 36.

It should be noted, in conclusion, that there occur in nature two kinds of particles that can be distinguished from each other by their statistical properties in a collective, *fermions* and *bosons*.

Fermions behave according to an important law—the *Pauli exclusion principle*. We consider it convenient to idealize somewhat the situation, formulating the Pauli exclusion principle in the following way (it will be formulated more exactly in Sec. 39). A system of N identical fermions can contain in any phase volume Γ only a finite number of representative points, not exceeding some integer $N_{\max}(\Gamma)$. The number $N_{\max}(\Gamma)$ decreases uniformly as the considered phase volume Γ diminishes, as shown in Fig. 52. Thus, the phase volume confined between na and $(n+1)a$ can contain no more than n points representing the state of a fermion. It should be stressed that these

results do not depend on the form of the phase volume under consideration, but only on its size.

Assume now the minimum phase volume per representative point to be the volume of an elementary cell in the μ-space, both for fermions and for bosons. It will soon become clear that the quantity a is determined uniquely by the laws of nature and can be found experimentally*.

The Pauli exclusion principle can now be formulated as follows: in a system of N identical fermions one cell in the μ-space can contain *no more* than one representative point.

In contrast to the foregoing, in a system of N identical bosons a μ-space cell can contain *any* number of representative points from zero to N.

The quantum field theory proves an important theorem—the *Pauli theorem*, relating the spin of a particle and the type of statistics that the particle obeys. According to this theorem, all particles with a half-integral spin are fermions (of the elementary particles they include electrons, positrons, protons, neutrons, μ-mesons, hyperons, etc.), while all particles with an integral spin are bosons (including among the elementary particles photons, π-mesons, K-mesons, etc.). As for compound particles (nuclei, atoms, molecules, ions), inasmuch as they include only particles with a spin $s = 1/2$, the following rule is valid for them: particles consisting of an even number of elementary particles are bosons, and those consisting of an odd number of elementary particles are fermions.

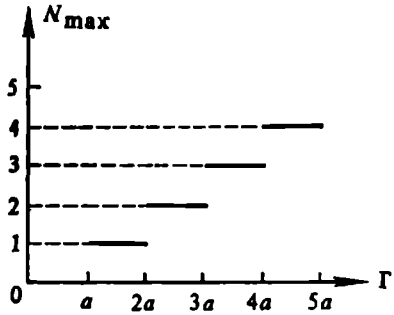


FIG. 52

It should be noted that in formulating the Pauli principle the presence of spin was ignored. It is well known that the states of a particle with spin are degenerate with a degeneracy multiplicity of $2s + 1$ (the projection of spin on some selected direction can have $2s + 1$ different values) and, therefore, it would be right to say that a cell in the μ-space can contain no more than $2s + 1$ representative points. We may, however, leave unchanged the statement of the

* According to Pauli's exclusion principle, the quantity a was already specified in principle. We may, however, imagine the existence of a Universe in which only bosons would exist, and no fermions. In such a Universe a would not be determined a priori; however, as will be shown below, natural laws dictate unambiguously the selection of the volume of a cell and a can all the same be found from experimental data.

Pauli principle and change the definition of the μ-space, adding to the coordinates x, y, z, ξ, η, ζ one more discrete variable, the projection of spin on the z-axis, acquiring $2s + 1$ values. This is equivalent to stating that in the old sense of the word each cell of the μ-space, determined by coordinates x, y, z, ξ, η, ζ does not exist alone, but that there are $2s + 1$ such cells.

Let us now illustrate the difference in the statistical properties of the different particles, fermions and bosons, by considering a simple example. Arrange two particles in three cells 1, 2, 3. If these particles are distinguishable from one another (they are then denoted by a and b), nine different arrangements depicted in Fig. 53 are possible. Six different arrangements are possible for bosons, due to their indistinguishability (indistinguishable particles are represented by crosses), as shown in Fig. 54. Due to the indistinguishability of fermions and by virtue of the Pauli principle, only three arrangements are possible for them, as shown in Fig. 55.

Having made these preliminary remarks, let us turn to the derivation of the most probable distributions, beginning with a system consisting of identical bosons.

Consider the ith box containing N_i bosons (Fig. 56). Taking $g_i - 1$ partitions and placing them arbitrarily, the box is subdivided into g_i cells. Thus, we have two classes of objects: particles and partitions. Denote by W_i the number of different ways of arranging N_i particles in g_i cells. Since the particles are assumed to be indistinguishable, these methods can differ from one another only in the number of particles in the cells when there is a fixed number of particles in the box, N_i; while the different methods can be obtained from each other by transfer of particles from cell to cell (by changing the position of particles and partitions). Having fixed each such distribution, let us carry out every possible permutation of particles (their number is equal to $N_i!$) and partitions (their number is equal to $(g_i - 1)!$) which give no new distribution. It is clear that we shall obtain as a result all possible permutations of a collective of $N_i + g_i - 1$ objects, including both particles and partitions, i.e.

$$N_i!\,(g_i - 1)!\,W_i = (N_i + g_i - 1)!,$$

whence

$$W_i = \frac{(N_i + g_i - 1)!}{N_i!\,(g_i - 1)!}. \tag{34.1}$$

When dealing with a number of boxes, the number of ways W of distributing the particles among the boxes so that the first box contains N_1 particles, the second N_2 particles, etc. is evidently equal to the product W_i. From this it follows that the main statistical formula for bosons is

$$W = \prod_i \frac{(N_i + g_i - 1)!}{N_i!\,(g_i - 1)!} \tag{34.2}$$

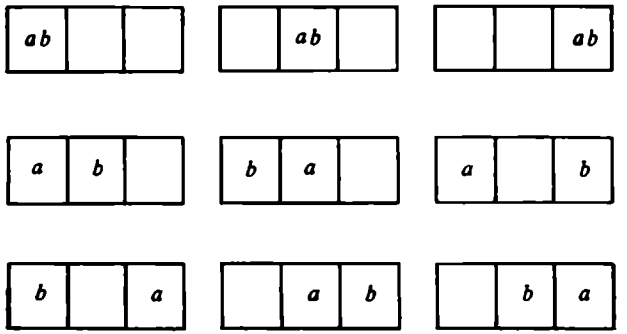


FIG. 53

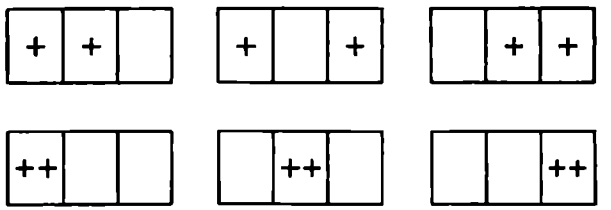


FIG. 54

FIG. 55

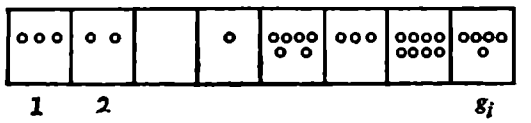


FIG. 56

Passing over to finding the most probable distribution, we must determine the maximum value of the quantity W. It is, however, more convenient to find the maximum of the quantity $\sigma = \ln W$. Making use of Stirling's formula for the factorials of large numbers (see the Mathematical Appendix, AII), we obtain at $N_i \gg 1$ and $g_i \gg 1$

$$\sigma = \ln W = \sum_i [\ln (N_i + g_i - 1)! - \ln N_i! - \ln (g_i - 1)!]$$

$$\approx \sum_i [(N_i + g_i) \ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i]. \quad (34.3)$$

Let us look for the maximum of the quantity σ under two supplementary conditions: the total number of gas particles is given by

$$\sum_i N_i = N \quad (34.4)$$

and the total energy of the gas is fixed:

$$\sum_i N_i \varepsilon_i = U. \quad (34.5)$$

Using the Lagrangian method of multipliers (AIII), let us equate to zero the derivatives of the quantity $\Phi = \sigma + \alpha N - \beta U$, where α and β are Lagrangian multipliers,

$$\frac{\partial \Phi}{\partial N_i} = \ln (N_i + g_i) - \ln N_i + \alpha - \beta \varepsilon_i = 0.$$

It follows from the above that the most probable number of particles in a cell is expressed by the formula

$$N_i = \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} - 1}. \quad (34.6)$$

The distribution expressed by formula (34.5) was derived in 1924 by A. Einstein and is referred to as the *Bose-Einstein distribution* (R. C. Bose derived it for the particular case of a photon quantum gas). The parameters α and β are specified by the conditions (34.4) and (34.5), which after Eq. (34.6) is substituted, acquire the form

$$\sum_i \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} - 1} = N, \quad (34.7)$$

$$\sum_i \frac{g_i \varepsilon_i}{e^{-\alpha + \beta \varepsilon_i} - 1} = U. \quad (34.8)$$

The physical corollaries of the Bose-Einstein distribution will be discussed below.

Let us turn now to the derivation of the distribution for fermions, the *Fermi-Dirac distribution*. Consider the ith energy box with n

number of cells g_i and a number of particles N_i (according to the Pauli principle $N_i \leqslant g_i$) depicted in Fig. 57. Since the particles are indistinguishable, the different ways of distribution differ from each other only in that some cells are occupied by one particle and some cells are empty, or, in other words, in the permutations of empty cells

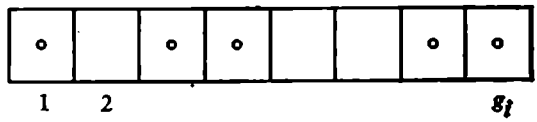


FIG. 57

with occupied ones. Having fixed such a distribution, let us carry out all possible permutations without adopting any new methods of distribution of N_i occupied cells and $g_i - N_i$ empty cells. Having made these permutations, we obtain the total number of permutations $g_i!$ among cells:

$$N_i!\,(g_i - N_i)!\,W_i = g_i!,$$

whence the number of ways of particle arrangement is

$$W_i = \frac{g_i!}{N_i!\,(g_i - N_i)!}. \tag{34.9}$$

The total number of ways of distribution of N particles among all boxes, observing condition that N_i particles occupy the ith box, is

$$W = \prod_i \frac{g_i!}{N_i!\,(g_i - N_i)!}. \tag{34.10}$$

Making use of Stirling's formula, find $\sigma = \ln W$:

$$\sigma = \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)]. \tag{34.11}$$

Under the conditions stipulated by Eqs. (34.4) and (34.5), we find the maximum of the quantity σ, using the Lagrangian method. For this purpose we equate to zero the derivatives of the quantity $\Phi = \sigma + \alpha N - \beta U$:

$$\frac{\partial \Phi}{\partial N_i} = -\ln N_i + \ln (g_i - N_i) + \alpha - \beta \varepsilon_i = 0,$$

whence we obtain for the occupation numbers N_i

$$N_i = \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} + 1}. \tag{34.12}$$

Formula (34.12) differs from the corresponding expression (34.6) in the Bose-Einstein statistics only in the sign in front of unity in the denominator. The parameters α and β are specified by conditions

$$\sum_i \frac{g_i}{e^{-\alpha+\beta\varepsilon_i}+1} = N, \tag{34.13}$$

$$\sum_i \frac{g_i\varepsilon_i}{e^{-\alpha+\beta\varepsilon_i}+1} = U. \tag{34.14}$$

35. The Boltzmann Principle

To impart a physical content to statistical distributions (34.6) and (34.12), it is necessary to ascertain the physical meaning of the parameters α and β that are formally defined by the equations (34.7), (34.8) or (34.13), (34.14). For this purpose it is necessary to add to the investigation methods of statistical physics one more important physical postulate.

There exists a far-reaching similarity between the concept of entropy, introduced in thermodynamics in a purely phenomenological manner, and the function $\sigma = \ln W$ that appeared in deriving the statistical distributions.

Firstly, this similarity appears in the fact that, like entropy in thermodynamics, the function σ is additive. In fact, if we mentally subdivide the volume of a gas into parts, the number of ways in which all its molecules can be distributed among the energy boxes is equal to the product of the number of these ways for each part. Thus, W is a multiplicative function, and its logarithm an additive function.

Secondly, as was ascertained in thermodynamics, the entropy of an isolated system increases in equalization processes and reaches a maximum value in a state of equilibrium. Since we identify a state considered to be an equilibrium one from the viewpoint of thermodynamics with the state in which the distribution of particles among the cells of the phase μ-space is the most probable, then in that state the quantity $\sigma = \ln W$ also assumes a maximum value.

These arguments make it reasonable to postulate that with a degree of accuracy up to a constant multiplier thermodynamically defined entropy coincides with the quantity σ. If we assume the numerical coefficient to be equal to Boltzmann's constant $k = 1.38 \times \times 10^{-23}$ J/deg, i.e. determine entropy by the formula

$$S = k \ln W,$$

our choice leads to the coincidence of the quantity S with thermodynamic entropy.

In statistical physics it is convenient to use another definition of entropy,

$$S = \ln W, \tag{35.1}$$

according to which entropy is assumed to be a dimensionless quantity. Since the product $T\,dS$ must have the dimension of energy [formula $\delta Q = T\,dS$ will be assumed to be valid when determining entropy by formula (35.1)], then temperature must be measured not in the degrees of the absolute scale, but in energy units (kT is replaced by T), preserving in doing so the former notations S and T for the dimensionless entropy and the "energy" temperature. Equation (35.1) expresses the *Boltzmann principle.*

The entropy of a system in a state of equilibrium is

$$S_{\max} = \ln W_{\max} \tag{35.2}$$

(below we shall denote the entropy in a state of equilibrium simply by S). Since $W < W_{\max}$, then $S < S_{\max}$ as well.

Thus, according to Boltzmann, the increase in entropy in an equalization process is the result of the system passing from a less probable states to the most probable state.

The fundamental difference between the statistical interpretation of an irreversible process and the interpretation given by thermodynamics must be emphasized. From the viewpoint of phenomenological thermodynamics, in the case of an irreversible process a reverse process is impossible by definition. From the point of view of statistical physics a process reverse in respect to one that is thermodynamically irreversible is a transition from the most probable distribution to a less probable. Considerable fluctuations occur very rarely in a macroscopic system and their probability is low. In systems comprising a small number of particles the probability of even large fluctuations is considerable and fluctuations occur quite often.

It will now be shown how the Boltzmann principle can be used in finding the physical meaning of the parameters α and β.

We shall make use of formulae

$$\sum_i \frac{g_i}{e^{-\alpha+\beta\varepsilon_i} \mp 1} = N, \quad \sum_i \frac{g_i\varepsilon_i}{e^{-\alpha+\beta\varepsilon_i} \mp 1} = U \tag{35.3}$$

(the upper sign pertains to the Bose-Einstein distribution, and the lower to the Fermi-Dirac distribution) relating, thereby, the entropy in an equilibrium state with the number of particles N and the internal energy U.

Let us make the following preliminary methodological comment. All cells pertaining to the same box are equivalent. This is clear, in particular, from the fact that the number of particles in the box N_i is proportional to g_i in both the Bose-Einstein distribution (34.6) and the Fermi-Dirac distribution (34.12). Therefore, it is often expe-

dient to use the occupation numbers related to one cell, $n_i = N_i/g_i$. These numbers are equal to

$$n_i = \frac{1}{e^{-\alpha+\beta\varepsilon_i} \mp 1} \tag{35.4}$$

the minus and plus signs relating to systems of bosons and fermions respectively. Making use of the numbers n_i, any sums over the "boxes" will be reduced to the form $\sum_i g_i F(i)$, where $F(i)$ is a function of the box number. When presented in this form the equivalence of the cells manifests itself clearly due to the presence of the multiplier g_i.

Let us now find the equilibrium-state entropy, first for a system of bosons. Making use of formula (34.3) and introducing the numbers n_i, we obtain

$$S = \sum_i [(N_i + g_i) \ln (N_i + g_i) - N_i \ln N_i - g_i \ln g_i]$$

$$= \sum_i g_i [(n_i + 1) \ln (n_i + 1) - n_i \ln n_i]. \tag{35.5}$$

The maximum value of the entropy can be found substituting the value of n_i from the Bose-Einstein distribution:

$$S = \sum_i g_i \left[\frac{-\alpha+\beta\varepsilon_i}{e^{-\alpha+\beta\varepsilon_i}-1} - \ln (1 - e^{\alpha-\beta\varepsilon_i}) \right]. \tag{35.6}$$

Using formulae (35.3), we finally find that

$$S = -\alpha N + \beta U - \sum_i g_i \ln (1 - e^{\alpha-\beta\varepsilon_i}). \tag{35.7}$$

By analogy, with the aid of formula (34.11) we find for a system of fermions that the entropy

$$S = \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)]$$

$$= -\sum_i g_i [(n_i \ln n_i + (1 - n_i) \ln (1 - n_i)]. \tag{35.8}$$

Substituting the equilibrium distribution described by formula (35.4), we obtain the expression for the maximum entropy

$$S = \sum_i g_i \left[\frac{-\alpha+\beta\varepsilon_i}{e^{-\alpha+\beta\varepsilon_i}+1} + \ln (1 + e^{\alpha-\beta\varepsilon_i}) \right] \tag{35.9}$$

and, making use of formulae (35.3),

$$S = -\alpha N + \beta U + \sum_i g_i \ln (1 + e^{\alpha-\beta\varepsilon_i}). \tag{35.10}$$

Combining the two results, we obtain the formula

$$S = -\alpha N + \beta U \mp \sum_i g_i \ln (1 \mp e^{\alpha - \beta \varepsilon_i}), \qquad (35.11)$$

where the minus sign relates to a system of bosons, and the plus sign to a system of fermions.

The following extremely important difference between the entropy formulae (35.5) and (35.8), on the one hand, and (35.7), (35.10), (35.11) on the other, must be emphasized. Formulae (35.5) and (35.8) determine the entropy of a gas in both an arbitrary equilibrium and non-equilibrium state. By contrast, formulae (35.7), (35.10), (35.11) pertain only to the equilibrium state of a gas with a maximum entropy and most probable occupation numbers $n_1, n_2, \ldots$. The entropy of the non-equilibrium state can be seen to be a function of an infinite set of occupation numbers n_i, related by the conditions $\sum_i g_i n_i = N$ and $\sum_i g_i n_i \varepsilon_i = U$ and arbitrary in all other respects. In contrast to this, the equilibrium-state entropy is fully defined by presetting the two parameters α and β, acquiring, thereby, a fundamental value in equilibrium thermodynamics.

In order to establish the physical meaning of the parameters α and β, let us find the differential of entropy from formula (35.11) and compare it with the expression dS used in thermodynamics. For this purpose we differentiate Eq. (35.11), first with respect to α at $\beta = \text{const}$, and then with respect to β at $\alpha = \text{const}$, assuming each time that $\varepsilon_i = \text{const}$, $g_i = \text{const}$.

In the absence of applied fields (electric, magnetic, gravitational, etc.) the levels of energy ε_i and the multiplicity factors of g_i depend only on the size of the vessel holding the gas (Sec. 45), i.e. on the parameter V. When applied fields are present, the energy levels also depend on other external parameters, or more exactly, on the intensity of the applied fields. Assume that no external fields of any kind are present, except the field of the vessel walls. The conditions $\varepsilon_i = \text{const}$ and $g_i = \text{const}$ are then equivalent to the condition $V = \text{const}$; therefore,

$$\left(\frac{\partial S}{\partial \beta}\right)_{\alpha, V} = -\alpha \left(\frac{\partial N}{\partial \beta}\right)_{\alpha, V} + U + \beta \left(\frac{\partial U}{\partial \beta}\right)_{\alpha, V} - \sum_i \frac{g_i \varepsilon_i}{e^{-\alpha + \beta \varepsilon_i} \mp 1}$$

and, consequently, according to formula (35.3),

$$\left(\frac{\partial S}{\partial \beta}\right)_{\alpha, V} = -\alpha \left(\frac{\partial N}{\partial \beta}\right)_{\alpha, V} + \beta \left(\frac{\partial U}{\partial \beta}\right)_{\alpha, V}. \qquad (35.12)$$

By analogy, using formula (35.3), we find

$$\left(\frac{\partial S}{\partial \alpha}\right)_{\beta, V} = -N - \alpha \left(\frac{\partial N}{\partial \alpha}\right)_{\beta, V} + \beta \left(\frac{\partial U}{\partial \alpha}\right)_{\beta, V} + \sum_i \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} \mp 1}$$

$$= -\alpha \left(\frac{\partial N}{\partial \alpha}\right)_{\beta, V} + \beta \left(\frac{\partial U}{\partial \alpha}\right)_{\beta, V}. \qquad (35.13)$$

Multiplying Eq. (35.12) by $d\beta$ and Eq. (35.13) by $d\alpha$ and summing, we obtain

$$dS_V = -\alpha\, dN + \beta\, dU. \tag{35.14}$$

On the other hand, it follows from the thermodynamic identity for the differential of internal energy,

$$dU = T\, dS - P\, dV + \mu\, dN,$$

that

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

and at a constant volume

$$dS_V = -\frac{\mu}{T} dN + \frac{1}{T} dU. \tag{35.15}$$

Comparing formulae (35.14) and (35.15), we find the physical meaning of α and β:

$$\beta = \frac{1}{T}, \tag{35.16}$$

$$\alpha = \frac{\mu}{T}. \tag{35.17}$$

The reader's attention is directed to the fact that in statistical physics we mean by N and dN the numbers of particles and not the numbers of moles, as in thermodynamics. Accordingly, in all following sections the chemical potential μ does not refer to one mole of substance, as in thermodynamics, but to one particle, so that the relationship $\mu_{\text{therm}} = N_A \mu_{\text{stat}}$ is true. We shall, nevertheless, retain the symbol μ for the chemical potential normalized to one particle. Substituting the expressions for β and α into formula (35.11) and taking into account the relationship $\Phi = \mu N$ and $F = U - TS = \Phi - PV$, we obtain

$$\frac{F-\Phi}{T} = \pm \sum_i g_i \ln (1 \mp e^{(\mu - \varepsilon_i)/T}), \tag{35.18}$$

whence we find the equation of state of Bose- and Fermi-gases:

$$PV = \mp T \sum_i g_i \ln (1 \mp e^{(\mu - \varepsilon_i)/T}). \tag{35.19}$$

The right-hand side of formula (35.19) is always positive, since with the upper sign (the Bose-Einstein statistics) the logarithm is negative.

Thus, the Bose-Einstein and the Fermi-Dirac distributions can be rewritten to read

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/T} \mp 1}, \tag{35.20}$$

and the supplementary conditions, keeping the number of particles and the total energy fixed, can be presented in the form

$$\sum_i \frac{g_i}{e^{(\varepsilon_i-\mu)/T} \mp 1} = N, \quad \sum_i \frac{g_i \varepsilon_i}{e^{(\varepsilon_i-\mu)/T} \mp 1} = U. \tag{35.21}$$

It should be noted that once the physical meaning of the parameters α and β is defined, the physical interpretation of relationships (35.3) must be significantly changed. The first of these equations specifies, as before, the chemical potential μ as a function of the number of particles N and temperature T. The parameter $\beta = 1/T$, however, requires no supplementary definition. For this reason the second relationship defines the internal energy U as a function of μ and T, whereas the first relationship permits one, in principle, to find μ as a function of N and T. Thus, Eqs. (35.21) determine the internal energy U as a function of the number of particles N and temperature T. In particular, for a homogeneous system to which no external field is applied, the chemical potential μ and the energy referred to one particle, U/N, are, like all intensive quantities, functions of density N/V and temperature T.

Let us revert now to formula (35.11) and consider in greater detail a system in the presence of an external field. In contrast to the case considered above, in which the walls of the vessel constituted a field and the energy levels ε_i depended on the extensive parameter V, in the presence of other fields the quantities ε_i are functions of intensive parameters, i.e. of the intensities of corresponding fields. Therefore, the internal energy U can be considered to be a function of its natural parameters S, V, N and of the intensity of the field involved. In the presence of a magnetic field it will be assumed that $U = U(S, V, N, H)$.

In further discussion the definitions of free energy, heat content (enthalpy) and chemical potential, $F = U - TS$, $W = U + PV$, $\Phi = U - TS + PV$, will be retained and they will be assumed to depend both on their natural arguments and on field intensities. It is then clear that formulae (35.16) through (35.21) remain valid for this more general case, when the energy levels ε_i are functions of field intensity.

In concluding this section we will make the following remark. The derivation of the Bose-Einstein and Fermi-Dirac distributions by the boxes-and-cells method presupposes that while thermodynamic equilibrium sets in, the particles may change their energy, by passing from one box to another. Otherwise any initial non-equilibrium particle distribution in the μ-space would remain unchanged and would not relaxate to an equilibrium state, and the maximizing of $\ln W$ would be meaningless. It is clear the passage of particles from one box to another becomes possible owing to interaction of

the particles with the surroundings (there is no interaction between particles). This surrounding medium must be a thermostat ($T = \text{const}$) with impermeable ($N = \text{const}$) walls. This follows from the fact that in deriving the statistical distributions the total number of particles N and the total energy U are assumed to be fixed; with a fixed number of particles N the total energy U of an ideal gas depends only on temperature. Thus, the Bose-Einstein and the Fermi-Dirac distributions and also the Maxwell-Boltzmann distribution that will be derived in the following section represent the most probable distributions of particles of an ideal gas in the μ-space, on the condition that the gas is placed in a thermostat.

Problem

Using formulae (35.5) and (35.8), derive the Bose-Einstein and the Fermi-Dirac distributions, minimizing the free energy with the condition that $N = \text{const}$.

36. The Maxwell-Boltzmann Distribution

Let us consider now the corollaries of the hypothesis on the distinguishability of identical particles. We are dealing as before with a system of boxes with energy ε_i and a number of cells g_i, the problem being to arrange in the ith box N_i distinguishable particles. First, let us find the number of ways in which N particles can be arranged among these boxes without fixing the cells into which the particles are placed during the arrangement. Since the particles are assumed to be distinguishable, the different ways of achieving this distribution differ from one another in the permutations of particles found in different boxes. Denote the number of different ways by W'. Having carried out for each of the methods all possible permutations of particles inside each box, without introducing any new methods of distribution, we clearly obtain the total number of permutations of N particles, whence

$$W' \prod_i N_i! = N!, \quad W' = \frac{N!}{\prod_i N_i!}.$$

Let us find the number of ways in which N_1 distinguishable particles can be distributed among g_1 cells of the first box, N_2 particles among g_2 cells of the second box, etc. Since for each of the N_i particles of the ith box there exist, irrespective of the remaining boxes, g_i possible arrangements among the cells, the required number of ways is equal to $g_i g_i \ldots g_i = g_i^{N_i}$, and for all boxes equals $\prod_i g_i^{N_i}$. It follows that the total number of ways in which N particles can be distributed

among the boxes is equal to

$$W = W' \prod_i g_i^{N_i} = N! \prod_i \frac{g_i^{N_i}}{N_i!}. \tag{36.1}$$

Using Stirling's formula, we obtain for $\sigma = \ln W$ the expression

$$\sigma = N \ln N + \sum_i [N_i \ln g_i - N_i \ln N_i]. \tag{36.2}$$

The maximum of σ must be found under supplementary conditions

$$\sum_i N_i = N, \quad \sum_i N_i \varepsilon_i = U.$$

Making use again of the method of Lagrangian multipliers for finding the most probable distribution, we equate to zero the derivatives of the quantity $\Phi = \sigma + (\alpha + 1) N - \beta U$ with respect to N_i:

$$\frac{\partial \Phi}{\partial N_i} = \ln g_i - \ln N_i + \alpha - \beta \varepsilon_i = 0,$$

from which we obtain the Maxwell-Boltzmann distribution

$$N_i = g_i e^{\alpha - \beta \varepsilon_i}. \tag{36.3}$$

The parameters α and β, as before, are determined by the conditions

$$\sum_i g_i e^{\alpha - \beta \varepsilon_i} = N, \tag{36.4}$$

$$\sum_i g_i \varepsilon_i e^{\alpha - \beta \varepsilon_i} = U. \tag{36.5}$$

[*Note*: when finding the maximum of the quantity σ the term $N \ln N$ was not differentiated with respect to N_i. It can be easily ascertained by the reader that such differentiation changes only the magnitude of the parameter α, which all the same is found from conditions (36.4), (36.5).] It is clear that the Maxwell-Boltzmann distribution can be obtained as a limiting case of the Bose-Einstein and Fermi-Dirac distributions (35.20):

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/T} \mp 1}.$$

If for any ε_i the condition

$$e^{(\varepsilon_i - \mu)/T} \gg 1 \tag{36.6}$$

is satisfied, the unity in the denominator of this expression can be ignored and we obtain the Maxwell-Boltzmann distribution

$$N_i = g_i e^{(\mu - \varepsilon_i)/T}, \quad n_i = \frac{N_i}{g_i} = e^{(\mu - \varepsilon_i)/T}. \tag{36.7}$$

This result could be foreseen from simple physical considerations: the inequality (36.6) is equivalent to the inequality $\frac{N_i}{g_i} \ll 1$ and represents the gas rarefaction requirement. In a rarefied gas the average interparticle distances are large, and in this situation the particle distinguishability or indistinguishability requirement becomes immaterial—in practice the particles do not draw closer to one another and they cannot be "confused". It is natural then that in these conditions the statistical distributions for indistinguishable particles coincide with the distribution for distinguishable particles, i.e. the Maxwell-Boltzmann distribution.

Let us return now to the question raised in the beginning of Sec. 34, whether particles of a single type (electrons, photons, atoms, etc.) are identical or can they differ slightly from one another. The answer to this question follows from the fact that, as is shown by experimental results, the Bose-Einstein and the Fermi-Dirac distributions are valid for all particles, while the Maxwell-Boltzmann distribution is approximately true in the limiting case of small occupation numbers. This means that particles of a single type are indistinguishable and so identical.

The expression for the entropy of a gas in an arbitrary equilibrium or non-equilibrium state can be obtained in two ways.

1. From the expressions for the entropy of a boson (35.5) or fermion gas (35.8) it follows that at $n_i \ll 1$ [using the expansion $\ln(1 + x) \approx x$ at $x \ll 1$]

$$S = -\sum_i g_i n_i \ln n_i + N. \tag{36.8}$$

2. Using Boltzmann's formula $S = \ln W$, we obtain from (36.2)

$$S^* = -\sum_i g_i n_i \ln n_i + N \ln N. \tag{36.9}$$

[In expression (36.9) the "entropy" is denoted by S^*, since it differs from entropy S expressed by formula (36.8) in the term $N \ln N - N$.] The term $N \ln N$ in formula (36.9) makes the "entropy" S^* a non-extensive quantity, which returns us again to the Gibbs paradox, considered within the framework of phenomenological thermodynamics in Sec. 23 of this book.

Actually, if we mix r portions of a single gas at the same density and temperature, and wish to calculate the entropy of the mixture, N_i must be replaced by rN_i and N by rN, leaving n_i unchanged. As a result, the entropy defined by formula (36.8) increases r times and the total entropy of r portions of gas remains unchanged, while the "entropy" S^*, determined by formula (36.9) acquires, in addition to the multiplier r, the term $Nr \ln r$. Consequently, the mixing results in total entropy increasing by $Nr \ln r$. This is the essence of the so-called *Gibbs paradox*.

In the classical Boltzmann theory this disadvantage was formally "corrected", as suggested by Gibbs, in the following manner. The states of a gas differing from each other in the permutations of the representative points in the μ-space, physically indistinguishable due to the identity of molecules, are assumed to be a single state. This leads to the need to divide the number of ways W by the number of permutations of $N!$ molecules. Hence, $\ln N!$ must be subtracted from S^* and, according to Stirling's formula, the "entropy" S^* "corrected" in this manner coincides with the entropy S. (The formula describing the Maxwell-Boltzmann distribution does not change, since we changed $\ln W$ by the constant $N \ln N - N$.)

Gibbs' foresight is worthy of admiration, for as far back as the end of the nineteenth century he anticipated the present-day concept of the indistinguishability of particles. From the point of view of logic, however, the method used by Gibbs to eliminate the entropy paradox can in no way be considered consistent. Indeed, first, in the derivation of the Maxwell-Boltzmann distribution gas particles were considered to be distinguishable and only in the final result is a "correction" introduced, accounting for the identity of states differing from each other in the permutations of molecules. A logically consistent method of reasoning would be based on the particle indistinguishability hypothesis and would lead to the Bose-Einstein or Fermi-Dirac distributions. But the Maxwell-Boltzmann distribution appears in this case as an approximate distribution in the limiting case of small occupation numbers.

It should be noted that for the range of application of the Boltzmann distribution the inequality $N_i/g_i \ll 1$ is valid, and even at large numbers g_i the numbers N_i can be small or close to unity. Furthermore, as will be shown in Sec. 39, in which account will be taken of the discreteness of the atomic and molecular energy levels, known from quantum mechanics, the g_i numbers can be close to unity in certain conditions, mainly for low energy levels.

In these conditions the derivation of the statistical distributions in calculating $N_i!$ and $g_i!$ by Stirling's formula becomes incorrect. All the same the Bose-Einstein and Fermi-Dirac distributions, as well as the Maxwell-Boltzmann distribution for small cell occupation numbers N_i/g_i, derived by this method, are correct. This can be shown by comparing the corollaries stemming from these formulae with experimental results and is confirmed by the fact that all three distributions can be derived by methods other than the boxes-and-cells method and not based on the assumption that the numbers N_i and g_i are large compared with unity. One of these methods, the general Gibbs method, applicable not only to ideal gases but also to systems of interacting particles, will be discussed in detail in Ch. VI. The Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann distributions are then obtained as particular cases.

Problem

Using formula (36.8), derive the Maxwell-Boltzmann distribution, minimizing the free energy on condition that $N = \text{const}$.

37. Transition to Continuously Varying Energy. Degeneracy Conditions for Ideal Gases

We obtained above three statistical distributions.

1. The Bose-Einstein distribution

$$N_i = \frac{g_i}{e^{(\varepsilon_i-\mu)/T}-1}, \quad N = \sum_i \frac{g_i}{e^{(\varepsilon_i-\mu)/T}-1}, \quad U = \sum_i \frac{g_i\varepsilon_i}{e^{(\varepsilon_i-\mu)/T}-1}. \tag{37.1}$$

2. The Fermi-Dirac distribution

$$N_i = \frac{g_i}{e^{(\varepsilon_i-\mu)/T}+1}, \quad N = \sum_i \frac{g_i}{e^{(\varepsilon_i-\mu)/T}+1}, \quad U = \sum_i \frac{g_i\varepsilon_i}{e^{(\varepsilon_i-\mu)/T}+1}. \tag{37.2}$$

3. The Maxwell-Boltzmann distribution

$$N_i = g_i e^{(\mu-\varepsilon_i)/T}, \quad N = \sum_i g_i e^{(\mu-\varepsilon_i)/T}, \quad U = \sum_i g_i\varepsilon_i e^{(\mu-\varepsilon_i)/T}. \tag{37.3}$$

It should be emphasized that from the viewpoint of classical physics the energy, like any other dynamic quantity, varies continuously, acquiring any intermediate values. In deriving the statistical distributions the energy was only assumed for convenience to be a discretely varying quantity when we introduced the subdivision into energy layers (boxes). Let us now assume that the energy layers are sufficiently thin, this assumption allowing us to replace in the formulae specifying the chemical potential and the internal energy the summation over the boxes by integration. It should be noted here that since the variable multiplier present in the three distributions depends only on energy, the numbers of representative points in equal phase volumes of the same energy level are equal, and for a statistical description of a gas we can introduce the number of particles dN per element of phase volume $d\Gamma = \prod_i dq_i\, dp_i$, or the number of particles whose generalized coordinates lie within $(q_i,\ q_i + dq_i)$ and genera-

lized momenta within $(p_i, p_i + dp_i)$. Then the number of cells g_i must evidently be replaced by the expression

$$g\frac{d\Gamma}{a} = g\frac{\prod_i dq_i\,dp_i}{a},$$

where a = phase volume of one cell, introduced in Sec. 34;
g = weight factor.

The appearance of the weight factor is associated with the fact that when q_i and p_i are fixed, a particle can often be found in different states, with different parameters. If, for instance, the spin of a particle is s, the projection of the spin in some direction in space can have $2s + 1$ different values ($-s$, $-s + 1$, . . ., $s - 1$, s being measured in units of $h/2\pi$). In this case $g = 2s + 1$. For light quanta $g = 2$, since when the frequency ν and the propagation direction are fixed, the light quantum, photon, can have two independent directions of polarization.

Passing to the continuous description the statistical distributions will be rewritten as follows.

1. The Bose-Einstein distribution

$$dN = \frac{g}{a}\frac{d\Gamma}{e^{(\varepsilon-\mu)/T}-1}, \quad N = \frac{g}{a}\int\frac{d\Gamma}{e^{(\varepsilon-\mu)/T}-1}, \quad U = \frac{g}{a}\int\frac{\varepsilon\,d\Gamma}{e^{(\varepsilon-\mu)/T}-1}. \tag{37.4}$$

2. The Fermi-Dirac distribution

$$dN = \frac{g}{a}\frac{d\Gamma}{e^{(\varepsilon-\mu)/T}+1}, \quad N = \frac{g}{a}\int\frac{d\Gamma}{e^{(\varepsilon-\mu)/T}+1}, \quad U = \frac{g}{a}\int\frac{\varepsilon\,d\Gamma}{e^{(\varepsilon-\mu)/T}+1}. \tag{37.5}$$

3. The Maxwell-Boltzmann distribution

$$dN = \frac{g}{a}e^{(\mu-\varepsilon)/T}d\Gamma, \quad N = \frac{g}{a}\int e^{(\mu-\varepsilon)/T}d\Gamma, \quad U = \frac{g}{a}\int \varepsilon e^{(\mu-\varepsilon)/T}d\Gamma. \tag{37.6}$$

Pay attention to the following important distinction between the Bose-Einstein and Fermi-Dirac distribution and the Maxwell-Boltzmann distribution.

In the case of boson or fermion systems the second equations in (37.4) and (37.5) can be solved in principle with respect to μ, although in the general case this can be done only approximately, with μ then depending on N and T and also, parametrically, on the phase volume a of a cell. For this reason, after the values of the chemical

potential are substituted into the expressions for U (37.4) and (37.5), the internal energy will also depend on the number of particles, temperature and the parameter a. It follows from the foregoing that the quantity a can in principle be found by comparison with experiment carried out, for instance, in measuring heat capacity $C_V = (\partial U/\partial T)_V$.

The situation proves to be quite different when we use the formula describing the Maxwell-Boltzmann distribution. Let us pay attention to the fact that the chemical potential μ and the cell volume a are present in Eq. (37.6) as multipliers in the same form as $e^{\mu/T}/a$. Therefore the elimination of μ from the system of the two equations means at the same time the elimination of a. Consequently, the internal energy U is a function of N and T independent of a. Formula (37.6) yields the expression

$$U = N \frac{\int \varepsilon e^{-\varepsilon/T} d\Gamma}{\int e^{-\varepsilon/T} d\Gamma},$$

in which the phase volume a is not present.

In the case of the Bose-Einstein and Fermi-Dirac distributions the internal energy U is determined by formula

$$U = N \frac{\int \varepsilon \, d\Gamma \, (e^{(\varepsilon-\mu)/T} \mp 1)^{-1}}{\int d\Gamma \, (e^{(\varepsilon-\mu)/T} \mp 1)^{-1}}$$

and depends essentially on μ and, consequently, on a. Thus, as has already been mentioned above, for the exact statistical Fermi-Dirac and Bose-Einstein distributions the volume of an elementary cell, as was mentioned in Secs. 33 and 34, is not arbitrary, as is within certain limits the volume of a box; the volume of a cell is fixed exactly by laws of nature and can be found by experiment. This becomes impossible only in the limiting case of small occupation numbers (when the Maxwell-Boltzmann distribution is valid), and the phase volume of a cell acquires arbitrary values.

Let us now determine more exactly the criterion of validity of the Maxwell-Boltzmann distribution, considering, in particular, the case of a monoatomic ideal gas in the absence of an applied field:

$$\varepsilon = \frac{p^2}{2m} = \frac{\xi^2 + \eta^2 + \zeta^2}{2m}.$$

Since the energy depends only on the magnitude of the momentum vector, it is natural to subdivide the momentum space into spherical layers with a volume $4\pi p^2 \, dp$, whence we obtain for $d\Gamma$ the expression

$$d\Gamma = V \cdot 4\pi p^2 \, dp.$$

It is usually convenient to replace integration over momentum by integration over energy with the aid of the expression $p = (2m\varepsilon)^{1/2}$:

$$d\Gamma = V \cdot 2\pi (2m)^{3/2} \varepsilon^{1/2} \, d\varepsilon.$$

The condition of validity of the Maxwell-Boltzmann distribution is the fulfilment of the inequality $e^{(\mu-\varepsilon)/T} \ll 1$ at any ε, including $\varepsilon = 0$; the inequality then acquires the form

$$e^{\mu/T} \ll 1. \tag{37.7}$$

When this condition is satisfied we can find $e^{\mu/T}$ from formula

$$e^{\mu/T} = \frac{Na}{g}\left(\int e^{-\varepsilon/T}\, d\Gamma\right)^{-1}.$$

The integral in the denominator can be readily calculated:

$$J = \int e^{-\varepsilon/T}\, d\Gamma = V \cdot 2\pi\,(2m)^{3/2} \int_0^\infty e^{-\varepsilon/T}\varepsilon^{1/2}\, d\varepsilon$$

$$= V \cdot 4\pi\,(2mT)^{3/2} \int_0^\infty e^{-x^2}x^2\, dx,$$

and, finally, we find (see Mathematical Appendix, AIV)

$$J = V\,(2\pi mT)^{3/2}.$$

It follows that

$$e^{\mu/T} = \frac{Na}{gV\,(2\pi mT)^{3/2}}.$$

It will be shown below that for a monoatomic gas the volume a of an elementary cell equals h^3, where h is Planck's constant, the criterion of validity of the Maxwell-Boltzmann distribution thus reducing to (the factor $g \sim 1$ can be omitted)

$$\frac{N}{V}\left(\frac{h^2}{2\pi mT}\right)^{3/2} \ll 1. \tag{37.8}$$

Thus, the validity of the Maxwell-Boltzmann statistic is promoted by a small gas density, N/V, large molecular masses m and high temperatures T.

The reverse criterion

$$\frac{N}{V}\left(\frac{h^2}{8\pi mT}\right)^{3/2} \gtrsim 1 \tag{37.9}$$

is the condition for which the Maxwell-Boltzmann distribution is inapplicable, the gas obeying the Bose-Einstein or the Fermi-Dirac distribution. The gas is then said to be *degenerate* and criterion (37.9) is known as the *degeneracy criterion*.

Let us consider criterion (37.8) first for a gas consisting of ordinary atoms. Substituting the numerical values of h, $N/V \sim 10^{19}$ cm^{-3} and $m \sim (10^{-23}$ to $10^{-24})$ g, we obtain $T \gg 10^{-1}$ K. It follows that for ordinary gases at a pressure close to normal the Maxwell-Boltzmann distribution is a good approximation down to rather low temperatures.

It is different for gases consisting of lighter particles, for instance, for an electron gas in metals. For an electron $m \approx 10^{-27}$ g and the Maxwell-Boltzmann distribution is, therefore, inapplicable to an electron gas in metal up to temperature of about 10^4 to 10^5 K and, consequently, the gas is a degenerate one.

38. The Ω-Potential of Bose and Fermi Gases

It the absence of an applied field the integrals specifying the total number of particles and the internal energy of Bose- and Fermi gases are proportional to the volume:

$$N = \frac{g}{a} \int \frac{d\Gamma}{e^{(\varepsilon-\mu)/T} \mp 1} = \frac{g}{a} V \int \frac{4\pi p^2 dp}{e^{(\varepsilon-\mu)/T} \mp 1}, \tag{38.1}$$

$$U = \frac{g}{a} \int \frac{\varepsilon\, d\Gamma}{e^{(\varepsilon-\mu)/T} \mp 1} = \frac{g}{a} V \int \frac{\varepsilon 4\pi p^2 dp}{e^{(\varepsilon-\mu)/T} \mp 1}, \tag{38.2}$$

which is why relationship (38.1) determines μ as an implicit function of N/V and relationship (38.2) directly defines the internal energy as a function of μ, T and V. Eliminating μ from Eqs. (38.1) and (38.2) we can, in principle, find U as a function of the variables N, V and T. In both cases, however, U is found as a function of foreign variables (it should be recalled that for internal energy the natural or own, variables are entropy S, volume V and the number of particles N). This is inconvenient in a number of cases; for instance, it is impossible to determine the gas pressure P and its entropy S by differentiating the internal energy, and more intricate technique must be applied. It is, therefore, advantageous to introduce one more thermodynamic function, whose natural variables would be μ, T, V. Write down for this purpose the differentials of the free energy and of the thermodynamic potential, Eqs. (22.6) and (22.9):

$$dF = -S\,dT - P\,dV + \mu\,dN,$$
$$d\Phi = d(\mu N) = \mu\,dN + N\,d\mu$$

and subtract the second equation from the first:

$$d(F - \Phi) = -S\,dT - P\,dV - N\,d\mu.$$

Denoting the quantity $F - \Phi$ by Ω, we obtain

$$\Omega = F - \Phi = -PV, \tag{38.3}$$

the differential of the Ω-potential being expressed by

$$d\Omega = -S\,dT - P\,dV - N\,d\mu. \tag{38.4}$$

Formula (38.4) shows that the natural variables for the Ω-potential are T, V and μ and that the entropy, pressure and the number

particles can be found by differentiating:

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}, \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu} = -\frac{\Omega}{V}, \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \tag{38.5}$$

Let us now show how other thermodynamic functions, Φ, F, U, W, are expressed in terms of the Ω-potential. Using Eq. (38.5), we obtain for the quantity Φ the expression

$$\Phi = N\mu = -\mu\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \tag{38.6}$$

Formula $F = \Phi - PV = \Phi + \Omega$ yields

$$F = \Omega - \mu\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \tag{38.7}$$

Using formulae (38.7) and (38.5), from relationship $U = F + TS$ we obtain

$$U = \Omega - \mu\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} - T\left(\frac{\partial \Omega}{\partial T}\right)_{\mu, V}. \tag{38.8}$$

Finally, the definition $W = U + PV = U - \Omega$ is used to find

$$W = -\mu\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} - T\left(\frac{\partial \Omega}{\partial T}\right)_{\mu, V}. \tag{38.9}$$

All the above relationships are of a general nature and are applicable to any monovariant thermodynamic system.

For the particular case of ideal Bose- and Fermi gases, according to formula (35.18),

$$\Omega = -PV = \pm T \sum_i g_i \ln\left(1 \mp e^{(\mu - \varepsilon_i)/T}\right), \tag{38.10}$$

where the upper sign pertains to a system of bosons, and the lower to a system of fermions. Upon integration the expression for the Ω-potential acquires the form

$$\Omega = \pm gT \int \frac{d\Gamma}{a} \ln\left(1 \mp e^{(\mu - \varepsilon)/T}\right). \tag{38.11}$$

It will be shown below that the Ω-potential of a gas to which no external field is applied is simply related to the internal energy. Assume that the energy of a particle is expressed in terms of its momentum by the formula

$$\varepsilon = Bp^s, \quad B = \text{const}, \quad s = \text{const},$$

that covers both the case of non-relativistic particles ($\varepsilon = p^2/2m$, $s = 2$) and the case of relativistic particles ($\varepsilon = cp$, $s = 1$).

Integrating Eq. (38.11) over the volume, we find

$$\Omega = \pm \frac{4\pi g T}{a} V \int_0^\infty p^2 \ln (1 \mp e^{\mu - \varepsilon(p)/T})\, dp.$$

Integrating the above expression by parts and allowing for the fact that the term outside the integral sign becomes zero at both the lower and upper limits, we obtain

$$\Omega = -\frac{4\pi g}{3a} V \int_0^\infty \frac{p^3 (\partial \varepsilon / \partial p)\, dp}{e^{[\varepsilon(p)-\mu]/T} \mp 1} = -\frac{s}{3} \frac{4\pi g}{a} \int_0^\infty \frac{\varepsilon p^2\, dp}{e^{[\varepsilon(p)-\mu]/T} \mp 1}. \quad (38.12)$$

Comparing Eq. (38.12) with the formula of internal energy

$$U = \frac{4\pi g}{a} V \int_0^\infty \frac{\varepsilon p^2\, dp}{e^{[\varepsilon(p)-\mu]/T} \mp 1}, \quad (38.13)$$

we find the relationship that we are interested in:

$$\Omega = -\frac{s}{3} U. \quad (38.14)$$

For non-relativistic particles, in particular,

$$\Omega = -\frac{2}{3} U, \quad (38.15)$$

and for ultrarelativistic particles (e.g. photons)

$$\Omega = -\frac{1}{3} U. \quad (38.16)$$

It should be emphasized that together with formula (38.13) formulae (38.14) through (38.16) specify the Ω-potential as a function of natural variables T, V and μ. The entropy and pressure can, therefore, be found by formulae (38.5), differentiating Ω with respect to the variables T, V. The last formula of (38.5), $N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$, is usually used to find the chemical potential and for its subsequent elimination from the formulae for the internal energy, entropy and pressure.

It should be noted in conclusion that formulae (38.14) through (38.16) are also valid for the limiting case presented by the Maxwell-Boltzmann statistics. For instance, when applied to a Maxwell-Boltzmann gas of non-relativistic particles, the formulae

$$\Omega = -PV, \quad U = \frac{3}{2} NT, \quad \Omega = -\frac{2}{3} U$$

yield the equation of state $PV = NT$. The Ω-potential of a Maxwell-Boltzmann gas can be found from Eq. (38.10) by way of the limiting

transition $e^{\mu/T} \ll 1$. It equals

$$\Omega = -Te^{\mu/T} \sum_i g_i e^{-\varepsilon_i/T}. \tag{38.17}$$

Let us now consider a Bose- or Fermi gas in the presence of an applied field. Formula (38.3) holding true for the Ω-potential, we arrive as before at (38.10), but, in addition to the variables T, V and μ, the Ω-potential now depends on the intensity of the field applied to the gas.

Let us consider in greater detail the case of a gas placed in a magnetic field, also to be discussed in Sec. 59. Calculate the derivative $\left(\frac{\partial \Omega}{\partial H}\right)_{T,V,\mu}$. According to (38.10),

$$\left(\frac{\partial \Omega}{\partial H}\right)_{T, V, \mu} = \sum_i g_i n_i \frac{\partial \varepsilon_i}{\partial H}.$$

Since the derivative $\frac{\partial \varepsilon_i}{\partial H}$ is the magnetic moment of a particle in the ith energy state with an opposite sign, we obtain

$$\left(\frac{\partial \Omega}{\partial H}\right)_{T, V, \mu} = -MV, \tag{38.18}$$

where M is the magnetization. Thus, the differential of the Ω-potential is represented by the expression

$$d\Omega = -S\,dT - P\,dV - N\,d\mu - MV\,dH. \tag{38.19}$$

Problem

Find the first-order corrections to the chemical potential, pressure and heat capacity of slightly degenerate Bose- and Fermi gases ($e^{\mu/T} \ll 1$).

Answer. $e^{\mu/T} = \frac{N}{gV}\left(\frac{h^2}{2\pi mT}\right)^{3/2}\left[1 \mp \frac{N}{gV}\left(\frac{h^2}{4\pi mT}\right)^{3/2}\right]$,

$$\frac{\Delta P}{P} = \mp \frac{N}{16gV}\left(\frac{h^2}{\pi mT}\right)^{3/2}, \quad \Delta C_V = \pm \frac{3}{4}\frac{N}{g}\left(\frac{h^2}{2\pi mT}\right)^{3/2}.$$

(the upper sign pertains to bosons, and the lower to fermions. The pressure in a Bose gas decreases, and in a Fermi gas increases, as compared with a Maxwellian gas).

9. Energy Quantization. The Nernst Theorem

This section is devoted to the changes in the apparatus of statistical physics caused by an account for the requirements of the quantum-mechanical theory. It should be noted for one thing that the hypothesis on the indistinguishability of identical particles introduced

in Sec. 34 is in fact a corollary of quantum mechanics. Indeed, as established in quantum mechanics, the classical concept of the trajectory, or path, becomes inapplicable to microparticles, and the motion of a particle is described as the propagation of more or less extensive wave packets which generally spread in space with time. This makes it impossible to trace the motion of a selected particle and distinguish it from other identical particles. For this reason the criterion on the indistinguishability of particles is an integral part of quantum mechanics.

Another most important thesis of quantum mechanics, which is of paramount importance to statistical physics, consists in the fact that the energy of any system of particles in finite motion can acquire only quantized values ε_1, ε_2, ... In the general case these energy values are degenerate, i.e. for each value ε_i there exists not one but g_i different states. In this connection the transition from the quantum-mechanical theory to the classical one has two aspects, as shown in Fig. 58.

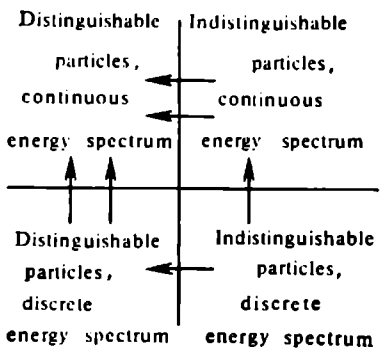

Distinguishable particles, continuous energy spectrum
Indistinguishable particles, continuous energy spectrum
Distinguishable particles, discrete energy spectrum
Indistinguishable particles, discrete energy spectrum

FIG. 58

1. With small occupation numbers, particles can be assumed approximately to be distinguishable and pass from the formulae describing the Bose-Einstein and Fermi-Dirac distributions to the formulae presenting the Maxwell-Boltzmann statistics. The possibility criterion for this transition was considered in Sec. 37.

2. The discreteness of the energy spectrum of real systems can be ignored, assuming energy to be a continuously varying quantity. It should be noted that this approximation was actually used in all preceding sections.

Let us now find the conditions that make such an approximation possible. Let the energy of a gas particle depend on the quantum number n, with the meaning of this number and the nature of the function $\varepsilon(n)$ depending on the particular problem. The physical meaning of the number n and the nature of the dependence $\varepsilon(n)$ will be shown below to differ for translational, rotational and vibrational motions. Energy quantization can evidently be ignored if the distances between neighbouring energy levels are small compared with the energy proper.

With large quantum numbers in all cases of practical interest $\varepsilon(n)$ is a homogeneous power function of the quantum number:

$\varepsilon(n) = An^{\alpha}$; then

$$\Delta\varepsilon(n) = A[(n+1)^{\alpha} - n^{\alpha}] \approx A\alpha n^{\alpha-1} = \alpha\frac{\varepsilon(n)}{n}.$$

The condition $\frac{\Delta\varepsilon}{\varepsilon} \ll 1$, therefore, leads to the inequality $n \gg 1$. Thus high levels are always closely arranged and energy can be assumed here to be a continuously varying quantity. Since at high temperatures most particles occupy high energy levels, energy quantization can be ignored in these conditions.

At low temperatures, however, a considerable fraction of particles occupy levels with $n \gtrsim 1$, the distances between levels being large and comparable to the magnitude of energy, and energy quantization becomes of essential importance. The exact meaning of the terms "high" and "low" temperatures is then established in the following manner. The energy of most gas particles is close to $\bar{\varepsilon} \propto T$. From this we find the values of the quantum number, n_{ef}, that are essential at the given temperature:

$$\varepsilon(n_{ef}) = An_{ef}^{\alpha} \propto T, \quad n_{ef} \propto \left(\frac{T}{A}\right)^{1/\alpha}.$$

Then the condition $n_{ef} \gg 1$ permits finding the characteristic temperature T_0, above which energy quantization is inessential; $T_0 \propto A$. It should be noted that the criterion $T \gg T_0 \propto A$ differs in the general case from the gas nondegeneracy condition

$$\frac{N}{V}\left(\frac{h^2}{2\pi mT}\right)^{3/2} \ll 1,$$

although both conditions are satisfied at high temperatures and for this reason a gas with discrete energy levels and a gas with continuously varying particle's energy can be both degenerate and nondegenerate.

Energy quantization is to be accounted for in the problems that will be presented in Secs. 44 through 48.

It should be noted that the derivation of the Bose-Einstein and Fermi-Dirac distributions and, consequently, the derivation of the Maxwell-Boltzmann distribution as their limiting case can be repeated without any changes and will lead us to the same results; however, the concepts of "boxes" and "cells" will then acquire another meaning.

By a box must now be meant an energy level, i.e. the totality of states of a particle with a given energy value, and by cells individual states with a given energy value. If the level is not degenerate (for a given energy value there corresponds only one state), then a cell coincides with a box, and if degeneracy exists, for the energy level, a box, there corresponds a greater or smaller number of cells. Quantum mechanics proves that the ground energy level, having lower

energy, is not degenerate as a rule. It should be noted that the theory accounting for energy quantization by no means requires that the numbers g_i should satisfy the condition $g_i \gg 1$, which must be met to permit application of Stirling's formula. For this reason the method of boxes and cells used to derive the Bose-Einstein and Fermi-Dirac distributions cannot, evidently, be applied here. However, as was already mentioned in Sec. 36, these distributions remain valid and they will be again derived in Sec. 64, applying another correct method.

Let us prove now the important *Nernst theorem* (already referred to in phenomenological thermodynamics, Sec. 10), according to which the entropy of a gas at $T = 0$ K is a constant quantity, independent of any variable parameters (pressure, volume, etc.). This constant will be shown to be equal to zero in many cases and therefore Nernst's theorem is usually formulated as follows:

$$S\,(T = 0) = 0, \tag{39.1}$$

although this statement fails to be universal.

The Nernst theorem holds both for bosons and fermions. Furthermore, if at $T = 0$ K the Maxwell-Boltzmann distribution were applicable to some particles, then this theorem would be true even for these non-existing particles, as it will be shown below. Since at sufficiently low temperatures a gas is actually always degenerate, this circumstance is of no practical use.

Let us turn to the proof of Nernst's theorem, departing from Boltzmann's formula (35.2) for the entropy in non-equilibrium states, $S = \ln W_{\max}$. Let us write down the formulae specifying the number of ways in which particles can be arranged over energy levels ε_i with generacy multiplicities g_i for fermions, bosons and classical (distinguishable) particles [(34.2), (34.10), (36.1)]:

$$\begin{aligned} W_f &= \prod_i \frac{g_i!}{N_i!\,(g_i - N_i)!}, \\ W_b &= \prod_i \frac{(N_i + g_i - 1)!}{N_i!\,(g_i - 1)!}, \\ W_{cl} &= N! \prod_i \frac{g_i^{N_i}}{N_i!}. \end{aligned} \tag{39.2}$$

The energy of a gas must be minimum at absolute zero; therefore, all the particles of the boson system and also the classical particles occupy the lowest energy level ($N_i = 0$, $i \neq 1$, $N_1 = N$), and in the fermion system the particles occupy n lowest energy levels, in accordance with the Pauli exclusion principle ($N_i = g_i$ at $i < n$, $N_i = 0$ at $i > n$, where $\sum_{i=1}^{n} N_i = N$; the level with $i = n$ can then

be occupied both partly and completely, $0 < N_n \leqslant g_n$). These distributions are shown in Fig. 59*a*, *b* where all g_i are for definiteness assumed to be equal to unity. Since in formulae (39.2) all the multipliers pertaining to the ith level become unity at $N_i = 0$ and at $N_i = g_i$ for a fermion system, at $T \to 0$, we get

$$W_f = \frac{g_n!}{N_n!\,(g_n - N_n!)}, \quad W_b = \frac{(N+g_1-1)!}{N!\,(g_1-1)!}, \quad W_{cl} = g_1^N. \tag{39.3}$$

Let us assume that the ground level ($g_1 = 1$) for a system of bosons or classical particles is not degenerate, and that in a system of fermions the level with $i = n$ ($g_n = 1$) is not degenerate. Then it is clear that in all three cases $W = 1$. The physical meaning of this

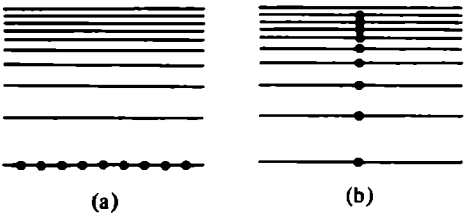


FIG. 59

result is obvious: under the conditions assumed the state of a gas is uniquely determined, since no particle permutations within one cell lead to a new state of the gas even for distinguishable particles. Consequently, we obtain the required result, expressed by formula (39.1), in accordance with Boltzmann's formula.

If the multiplicities g_1 and g_n are not equal to unity (this may occur, for instance, for particles having spin, when the multiplicities of any states are equal to $2s + 1$), the entropy at absolute zero is constant, though not equal to zero, as can be seen from formulae (39.3). For the case of bosons, for instance, using Stirling's formula, we have

$$S(T=0) = \ln \frac{(N+g_1-1)!}{N!\,(g_1-1)!} \approx (g_1 - 1) \ln N,$$

and for a system of classical particles

$$S\,(T = 0) = N \ln g_1.$$

All corollaries of Nernst's theorem (see Sec. 10) remain valid in this case as well, since they are based only on the fact that at absolute zero the entropy is independent of pressure, volume or of any other variable parameters.

It should be noted in conclusion that Nernst's theorem is also valid for a system of interacting particles (which will be proved in Sec. 63 within the framework of Gibbs' method).

CHAPTER IV

THE MAXWELL-BOLTZMANN GAS

The preceding chapter was devoted to the general statistical laws for any ideal gases both degenerate, obeying the Bose-Einstein and Fermi-Dirac distributions, and non-degenerate, described approximately by the Maxwell-Boltzmann distribution. Passing over to the solution of concrete problems, let us first consider an ideal Maxwell-Boltzmann gas. Although the model of a Maxwell-Boltzmann gas is an approximate one, it is applicable, as was shown in Sec. 37, to molecular and atomic gases down to very low temperatures. At the same time, it is considerably simpler to give a mathematical description of a gas by means of the Maxwell-Boltzmann distribution than with the aid of the Bose-Einstein and Fermi-Dirac distributions.

40. The Maxwell-Boltzmann Monoatomic Gas in the Classical Approximation. Phase Volume of a Cell and the Zero Point Entropy

This section is devoted to the discussion of a molecular ideal gas at sufficiently high temperatures permitting, firstly, to make use of the Maxwell-Boltzmann distribution and, secondly, to ignore the energy quantization.

We shall calculate the thermodynamic functions of the gas in this approximation, paying attention to the following important circumstance. In phenomenological thermodynamics (see Sec. 19), the internal energy U and the entropy S are determined accurate to the additive constants U_0 and S_0 (arbitrary selection of the zero points for the internal energy and entropy). The free energy F and the thermodynamic potential Φ are, therefore, determined in thermodynamics accurate to an arbitrary linear function of temperature, the heat content (enthalpy) W accurate to the additive constant, and only the Ω-potential can be defined uniquely in thermodynamics.

All thermodynamic potentials will be shown to be determined uniquely in statistical physics. The fact that the entropy S is determined uniquely in statistical physics already follows from Nernst's theorem (39.1). The entropy constant S_0 will be shown to be definitely related with the volume a of an elementary cell and, consequently, having determined the cell volume, we shall determine uniquely all thermodynamic potentials.

As was already shown in Sec. 37, the equations fixing the total number N of particles and the internal energy U in the Maxwell-Boltzmann approximation permit elimination of the chemical potential μ together with the cell volume a. The elimination results in

that we obtain for the internal energy the expression (37.19)

$$U = N \frac{\int \varepsilon e^{-\beta\varepsilon} d\Gamma}{\int e^{-\beta\varepsilon} d\Gamma}.$$

The expression in the denominator is called the *integral of states* (*statistical integral*) and is denoted by Z:

$$Z = \int e^{-\beta\varepsilon} d\Gamma. \tag{40.1}$$

It can easily be seen that the internal energy can be expressed in terms of the integral of states, since the expression in the numerator of U is equal to $-\frac{\partial Z}{\partial \beta}$. It follows that

$$U = -N \frac{\partial}{\partial \beta} (\ln Z).$$

Returning to the variable T, we obtain

$$U = NT^2 \frac{\partial}{\partial T} (\ln Z). \tag{40.2}$$

The heat capacity of the gas can be found by the formula $C_V = \left(\frac{\partial U}{\partial T}\right)_V$.

Thus, the internal energy of a gas is determined uniquely and the expression for it does not contain the cell volume a. In contrast to this the chemical potential although determined uniquely by the equation $N = g \int e^{\beta(\mu-\varepsilon)} \frac{d\Gamma}{a}$ as well, depends essentially on a:

$$e^{-\mu/T} = \frac{g}{Na} \int e^{-\varepsilon/T} d\Gamma = \frac{gZ}{Na}, \quad \mu = T \ln \left(\frac{Na}{gZ}\right). \tag{40.3}$$

By virtue of the formulae

$$\Phi = N\mu, \quad F = \Phi - PV, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V,$$

the cell volume a will also be present in the expressions for the thermodynamic potential, free energy and entropy, and, in particular, will determine the entropy zero point.

Let us now examine in greater detail the particular case of a monoatomic gas in the absence of an applied field. Then,

$$\varepsilon = \frac{p^2}{2m}, \quad d\Gamma = 4\pi p^2 \, dp \, dV = 2\pi (2m)^{3/2} \varepsilon^{1/2} \, d\varepsilon \, dV,$$

and the integral of states is expressed by

$$Z = 2\pi (2m)^{3/2} V \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/T} \, d\varepsilon.$$

Introducing the integration variable $x = \varepsilon/T$, we obtain

$$Z = 2\pi (2m)^{3/2} V \int_0^\infty x^{1/2} e^{-x}\, dx = (2\pi mT)^{3/2} V, \tag{40.4}$$

whence, according to Eq. (40.2), we find for the internal energy of a monoatomic gas the expression

$$U = \frac{3}{2} NT,$$

and for the heat capacity of the gas

$$C_V = \frac{3}{2} N.$$

Substituting the value of Z from formula (40.4) into the expression (40.3) for the chemical potential, we find

$$\mu = T \ln \left[\frac{Na}{gV (2\pi mT)^{3/2}} \right]. \tag{40.5}$$

Eliminating N by formula (40.5), we obtain for the Ω-potential the expression

$$\Omega = -\frac{2}{3} U = -NT = -\frac{gV}{a} (2\pi m)^{3/2} T^{5/2} e^{\mu/T}, \tag{40.6}$$

whence

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu} = \frac{gV}{a} (2\pi mT)^{3/2} \left[\frac{5}{2} - \frac{\mu}{T} \right] e^{\mu/T}.$$

Expressing μ/T in terms of N and T, according to (40.5), we finally find that

$$S = \frac{3}{2} N \ln (TV^{2/3}) + N \ln \left[\frac{g e^{5/2} (2\pi m)^{3/2}}{Na} \right]. \tag{40.7}$$

The variable terms in Eq. (40.7) can readily be shown to coincide with the variable terms present in the thermodynamic formula (4.5) for the entropy of an ideal gas at $\gamma = \frac{5}{3}$. The additive constant in (40.7) is specified by the cell volume a. It should be noted that the formula for entropy derived in this section, just as the formulae for other thermodynamic quantities derived here, is inapplicable at low temperatures. One should not, therefore, be surprised at the fact that, according to (40.7), as $T \to 0$ the entropy $S \to -\infty$, which contradicts the Nernst theorem. The thermodynamic functions of a gas at low temperatures must be calculated, taking into account the degeneracy in the gas, its non-ideality and the quantization of energy.

41. The Maxwell Distribution

This section is devoted to the translational motion of particles of a Maxwell-Boltzmann ideal gas, ignoring energy quantization. Formulae (37.6) yield the expression for the probability of finding the representative point in the volume element $d\Gamma$ of the μ-space:

$$dW = \frac{dN}{N} = \frac{e^{-\varepsilon/T}\, d\Gamma}{\int e^{-\varepsilon/T}\, d\Gamma} \tag{41.1}$$

where the expression in the denominator is the statistical integral Z. The considered gas will be assumed to consist of molecules each having an arbitrary number n of atoms. Since, however, only the translational motion of the molecules is of interest to us, of all the molecular generalized coordinates and momenta, we shall consider only three coordinates of the centre of mass, x, y, z, and the relevant projections of the molecular total momentum ξ, η, ζ, and express the energy of a molecule in the form

$$\varepsilon = \frac{p^2}{2m} + \mathcal{U}(x, y, z) + \varepsilon', \tag{41.2}$$

where $p^2 = \xi^2 + \eta^2 + \zeta^2$ = squared momentum of a molecule as a whole;

$\mathcal{U}(x, y, z)$ = the potential energy of a molecule in an applied field (assumed to be independent of molecular orientation);

ε' = energy of the remaining degrees of freedom, independent of x, y, z, ξ, η, ζ.

Integrating Eq. (41.1) over all degrees of freedom, except the translational, we shall find the probability that the centre of mass of a molecule is contained in volume dV and its momentum is in the range between p and $p + dp$. This probability separates into two factors: one depends only on the momentum, and the other only on coordinates:

$$dW = \frac{e^{-p^2/2mT} dV_p}{\int e^{-p^2/2mT} dV_p} \frac{e^{-\mathcal{U}(x, y, z)/T} dV}{\int e^{-\mathcal{U}(x, y, z)/T} dV}. \tag{41.3}$$

which means that the momentum and coordinate distributions of molecules are independent of each other. Integrating Eq. (41.3) over the coordinates, we obtain

$$dW(p) = \frac{e^{-p^2/2mT} dV_p}{\int e^{-p^2/2mT} dV_p}. \tag{41.4}$$

Having specified the element of volume in the momentum space by the formula $dV_p = 4\pi p^2\, dp$ and calculating the integral in the de-

nominator

$$4\pi \int_0^\infty e^{-p^2/2mT} p^2\, dp = (2\pi mT)^{3/2}, \tag{41.5}$$

we obtain the momentum distribution of molecules

$$dW_p = \frac{4\pi}{(2\pi mT)^{3/2}} e^{-p^2/2mT} p^2\, dp. \tag{41.6}$$

Passing from the momentum to velocity, we have

$$dW(v) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2\, dv. \tag{41.7}$$

Formulae (41.6), (41.7), corresponding to the Maxwell distribution, permit the solution of a number of concrete problems.

Let us find the most probable velocity v_p of gas molecules. For this velocity, formula (41.7) must assume a maximum value

$$\frac{d}{dv}(v^2 e^{-mv^2/2T}) = ve^{-mv^2/2T}\left(2 - \frac{mv^2}{T}\right) = 0, \tag{41.8}$$

whence

$$v_p = \sqrt{\frac{2T}{m}}. \tag{41.9}$$

The mean and mean square velocities can also be readily found:

$$\bar{v} = \int v\, dW(v) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2T}\, dv = \left(\frac{8T}{\pi m}\right)^{1/2}, \tag{41.10}$$

$$\bar{v^2} = \int v^2\, dW(v) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} \int_0^\infty v^4 e^{-mv^2/2T}\, dv = \frac{3T}{m}. \tag{41.11}$$

It follows from the foregoing that the energy of translational molecular motion is equal to

$$\bar{E}_k = \frac{m\bar{v^2}}{2} = \frac{3}{2} T.$$

The Maxwell distribution of molecular velocities is shown graphically in Fig. 60. With rising temperature the maximum of the curve shifts toward high temperatures and the curve itself runs steeper with a more considerable "tail" extending to the region of high velocities.

If the momentum space is cut not into spherical layers, but into parallelepipeds $dv_x\, dv_y\, dv_z$, the distribution can be presented as a product of three factors of the form

$$dW(v_i) = \left(\frac{m}{2\pi T}\right)^{1/2} e^{-mv_i^2/2T}\, dv_i \quad (i = x, y, z), \tag{41.12}$$

which indicates that the distributions of various components of velocity are independent. The Maxwell distribution of velocity projection is presented graphically in Fig. 61.

It is easily comprehended from physical considerations and can be checked by direct calculation that the mean value of the projections

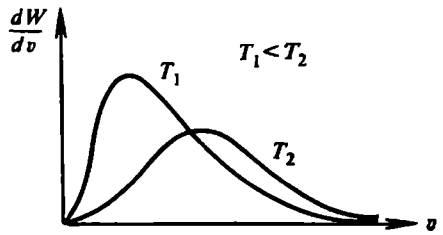


FIG. 60

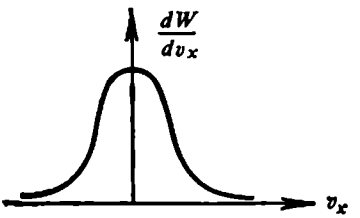


FIG. 61

v_x, v_y, v_z is equal to zero. The probability that the ith projection of velocity falls in the range between v_1 and v_2 is

$$W(v_1, v_2) = \left(\frac{m}{2\pi T}\right)^{1/2} \int_{v_1}^{v_2} e^{-mv^2/2T}\, dv,$$

and passing to the dimensionless variable $x = \frac{v}{v_p} = \sqrt{\frac{m}{2T}}\, v$, we get

$$W(v_1, v_2) = \frac{1}{2}[\operatorname{erf}(x_2) - \operatorname{erf}(x_1)], \tag{41.13}$$

where the function

$$\Phi(x) = \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \tag{41.14}$$

is referred to as the *probability integral* or the Gauss error function. It is not expressed in terms of elementary functions, but is well studied and tabulated [see, for instance, [5] where the notation $\Phi(x)$ is used instead of the symbol erf (x)].

The function erf (x) satisfies the boundary conditions erf $(0) = 0$ and erf $(\infty) = 1$. The function can readily be presented asymptotically at $x \ll 1$, expanding e^{-t^2} into a series and integrating it termwise. Then,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\, x \left(1 - \frac{1}{3}x^2 + \ldots\right). \tag{41.15}$$

At large values of x ($x \gg 1$) [see Mathematical Appendix, AV, formula (V.9)] we have

$$\operatorname{erf}(x) \approx 1 - \frac{e^{-x^2}}{\sqrt{\pi}\, x}. \tag{41.16}$$

The probability that the absolute value of velocity is in the range between v_1 and v_2 is also expressed in terms of the function erf (x). According to (41.7), we have

$$W(v_1, v_2) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} \int_{v_1}^{v_2} e^{-mv^2/2T} v^2\, dv$$

$$= \frac{4}{\sqrt{\pi}} \int_{x_1}^{x_2} e^{-t^2} t^2\, dt = -\frac{2}{\sqrt{\pi}} \int_{x_1}^{x_2} t\, d(e^{-t^2}),$$

where $x_i = \frac{v_i}{v_p} = \sqrt{\frac{2T}{m}}\, v_i$. Integrating the latter expression by parts, we obtain

$$W(v_1, v_2) = \frac{2}{\sqrt{\pi}} [x_1 e^{-x_1^2} - x_2 e^{-x_2^2}] + \operatorname{erf}(x_2) - \operatorname{erf}(x_1). \tag{41.17}$$

Problems

1. A plate having an area S moves with a velocity u in a rarefied gas in the direction making an angle α with the normal. Find the resistance force F, if the molecular collisions with the plate are elastic.

Answer. $F = 2nST [(1 + 2\xi^2 \cos^2 \alpha) \operatorname{erf}(\xi \cos \alpha)$

$+ \frac{2}{\sqrt{\pi}} \cos \alpha e^{-\xi^2 \cos^2 \alpha}]$, where $\xi = \frac{u}{v_p}$.

2. Find the density of particles $dj(v)$, flowing with a velocity v in a beam, escaping from a vessel through a small opening, and the total flux j. Calculate the average and the most probable molecular velocity in the beam and compare them with the same quantities for a gas confined in the vessel.

Answer. $dj(v) = n\pi \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^3\, dv$,

$$j = n \left(\frac{T}{2\pi m}\right)^{1/2} = \frac{n\bar{v}}{4}, \quad v_p = \left(\frac{3T}{m}\right)^{1/2},$$

$$\bar{v} = \left(\frac{9\pi T}{8m}\right)^{1/2}.$$

42. Spatial Distribution of Molecules

Let us return to Eq. (41.3) and integrate it with respect to momentum projections:

$$dW(x, y, z) = \frac{e^{-\mathcal{U}(x, y, z)/T}\, dx\, dy\, dz}{\int e^{-\mathcal{U}(x, y, z)/T}\, dx\, dy\, dz}. \tag{42.1}$$

Formula (42.1) describes the distribution in space of gas molecules, showing, as should have been expected, that gas molecules concentrate in space regions where the potential energy is minimum.

Let us consider a particular case of a gas placed in a gravitational field at altitudes small compared with the Earth radius, so that the potential energy $\mathcal{U}(z) = mgz$. Integrating Eq. (42.1) over x and y, we obtain

$$dW(z) = \frac{e^{-mgz/T}\, dz}{\int_0^\infty e^{-mgz/T}\, dz} = \frac{mg}{T} e^{-mgz/T}\, dz. \tag{42.2}$$

Using the obvious relationship

$$\frac{n(z)}{n(0)} = \frac{dW(z)}{dW(0)},$$

let us pass from the probability $dW(z)$ to $n(z)$, the number of molecules per unit volume at the altitude z. This yields

$$n(z) = n(0)\, e^{-mgz/T} \tag{42.3}$$

whence with the aid of the formula $P = nT$ we obtain

$$P(z) = P(0)\, e^{-mgz/T}. \tag{42.4}$$

Formulae (42.3) and (42.4) are called *barometric formulae*. It should, however, be noted that the corollaries stemming from these formulae, concerning the variation of pressure, density, chemical composition (dependence on m) with altitude are only applicable to a gas contained in a closed thermostat and cannot be applied in the case of the real atmosphere. This is owing to the fact that, firstly, the atmosphere is not an isothermal system and, secondly, it cannot be in statistical equilibrium.

The latter ascertion becomes obvious, if the approximate expression for the potential energy is replaced by the expression stemming from Newton's law of gravitation,

$$\mathcal{U}(r) = -\frac{\gamma mM}{r} = -\frac{mgR^2}{r},$$

where R is the average radius of the Earth spheroid.

Then, the probability density of finding a molecule at a distance r from the Earth's centre is expressed by

$$\frac{dW(r)}{4\pi r^2\, dr} \sim e^{mgR^2/rT}. \tag{42.5}$$

Expression (42.5) can be seen to remain finite as $r \to \infty$ and the normalizing integral $\int dW(r)$ is divergent, meaning that statistical equilibrium is impossible in a field that diminishes with distance as $1/r$, and that spreading of the atmosphere takes place for any planet.

The same conclusion can be arrived at in another manner. It is known that for a body to escape from the gravitational field of a planet, it must possess a velocity exceeding the escape velocity $v_2 = \sqrt{2gR}$. But according to Maxwell's distribution law, at any temperature there exists a "tail" extending over the region of velocities exceeding v_2. For this reason a fraction of molecules of the atmosphere continuously escapes from the planet, the fraction being the larger, the lower the escape velocity v_2.

Problems

1. Normalize the Boltzmann distribution for particles in a unidimensional field $\mathcal{U}(z) = kz^2/2$ and find $\bar{z}$ $(0 \leqslant z < \infty)$.

2*. Particles of a gas are in a central field of a potential $\mathcal{U}(r) = \begin{cases} \mathcal{U}_0 \ln(r/a), & r \leqslant a, \\ \infty, & r > a. \end{cases}$ Normalize Boltzmann's distribution. Find the heat capacity and pressure of the gas. Explain the paradox arising at low temperatures.

43. Polyatomic Gases (Classical Theory). The Equipartition Theorem

Let us apply the Maxwell-Boltzmann distribution to polyatomic gases. Formulae (40.1) and (40.2) remain valid, but by the quantities dV and dV_p in the expression for the volume in the μ-space, $d\Gamma = dV\, dV_p$, must now be meant the products of the differentials of all generalized coordinates and of all generalized momenta respectively.

In the absence of an applied field the energy of a molecule is equal to the sum of the kinetic energy, known from mechanics to be homogeneous quadratic function of momenta $a_{ik}p_ip_k$ (the coefficients a_{ik} generally depend on the generalized coordinates q_i) and the potential energy of atomic interaction. (Below, we shall follow the known Ein-

* The problem was suggested by G. L. Kotkin and V. G. Serbo.

stein condition, according to which repeated indices are summed.) Upon elimination of the translational and rotational motions of a molecule as a whole, the internal motion of atoms in a molecule is small oscillations about an equilibrium position, in which the potential energy is at a minimum. For this reason close to equilibrium the potential energy is a homogeneous quadratic function of generalized coordinates characterizing the molecular configuration, i.e. of all coordinates less those that describe the position and orientation of a molecule as a whole. The quantity $\mathcal{U}_{\min}$ is assumed to be the zero point for the potential energy and the equilibrium point, the origin of coordinates q_i. The number of these "internal" coordinates is equal to $3n - 5$ for an n-atomic molecule, if the molecule is linear (the equilibrium positions of atoms are arranged along one straight line), and to $3n - 6$, if the molecule is nonlinear. In fact, the position of a linear molecule is fully given by three coordinates x_c, y_c, z_c of the centre of inertia and two angles, while the orientation of a nonlinear molecule in space is given by three angles. Thus, the potential energy is expressed by the product $b_{rs}q_rq_s$, where b_{rs} are constant coefficients. It follows that

$$\varepsilon(q, p) = a_{ik}p_ip_k + b_{rs}q_rq_s,$$

and in the case of small deviations from equilibrium the coefficients a_{ik} can be assumed to be constant (in the above expression summation is carried out over i and k from 1 to $3n$, over r and s from 1 to $3n - 5$ in the case of linear molecules, and to $3n - 6$ for nonlinear molecules). By the foregoing we have

$$Z = BV \int e^{-a_{ik}p_ip_k/T} \prod_i dp_i \int e^{-b_{rs}q_rq_s/T} \prod_t dq_t.$$

The factor V appears in the above formula as a result of integration over the coordinates of the centre of mass of a molecule, and the constant dimensionless factor B as a result of integration over the angles specifying the molecular orientation in space.

To make explicit the dependence of this integral on temperature, the variable p_i is replaced by $P_iT^{1/2}$ and q_r by $Q_rT^{1/2}$, resulting in that the integrand becomes independent of T and the factor $T^{l/2}$, where l is the total number of differentials present in the integral for Z, is taken out of the integral sign. If a molecule contains n atoms, the number of generalized momenta equals $3n$ and the number of "internal" generalized coordinates is equal to $3n - 5$ or $3n - 6$. Consequently, $l = 6n - 5$ for a gas of linear molecules and $l = 6n - 6$ in the case of a gas of nonlinear molecules. In both cases l is the sum of the number of the translational and rotational degrees of freedom and of the doubled number of vibrational degrees of free-

dom. It follows from here that

$$Z = \text{const} \cdot T^{l/2},$$

and, according to formula (40.6), we obtain

$$U = NT^2 \frac{\partial}{\partial T} (\ln T^{l/2}) = \frac{l}{2} NT.$$

For one mole of a gas

$$U = \frac{l}{2} N_A T, \quad C_V = \frac{l}{2} N_A.$$

The obtained result can be formulated as the so-called *equipartition theorem*. Each translational and rotational degree of freedom contributes to the internal energy of one mole of a gas an amount of energy represented by the term $N_A T/2$ and into the molar heat capacity the term $N_A/2$; each vibrational degree of freedom contributes twice as much, i.e. the contribution is presented by the term $N_A T$ in the expression for the internal energy and by the term N_A in the expression for the heat capacity.

Thus, classical physics gives all kinds of intramolecular motion equal status (the contribution of the vibrational degrees of freedom is twice as high due to the presence of the potential energy, equal on the average to the vibrational kinetic energy, whereas the translational and rotational motions are associated with the presence of only kinetic energy). For monoatomic gases, in particular, classical theory predicts the following values: $C_V = \frac{3}{2} N_A$, $C_P = \frac{5}{2} N_A$, $\gamma = \frac{5}{3}$. It could appear at first sight that for monoatomic gases experimental results substantiate these predictions: the measured heat capacities of these gases are close to $\frac{3}{2} N_A$.

This agreement with experiment is, however, only apparent, for there is in fact a striking discrepancy between the prediction of classical theory and results of measurement. The point is that atoms are by no means material points with three degrees of freedom, but they consist of a nucleus, built from nucleons, and an electron shell. The actual number of degrees of freedom of an atom is, therefore, equal to $3(Z + A)$, where Z is the atomic number and A the number of nucleons in the nucleus. The measured heat capacity of monoatomic gases is, however, close to $\frac{3}{2} N_A$. This only indicates the fact that in contradiction with the laws of classical physics the electron and intranuclear degrees of freedom do not contribute to the heat capacity, i.e. they are "frozen". A similar situation is encountered in the case of polyatomic gases. If the electron and intranuclear degrees of freedom are ignored, the equipartition theorem predicts for all di-

atomic gases, for instance, the same heat capacity C_V equal to $\frac{7}{2} N_A$, whence $C_P = \frac{9}{2} N_A$ and $\gamma = \frac{9}{7}$. Experimental studies show, however, that at moderate temperatures $C_V = \frac{5}{2} N_A$, $C_P = \frac{7}{2} N_A$ and $\gamma = \frac{7}{5}$ for all diatomic gases. The heat capacity C_V diminishes with temperature and reaches the value of $\frac{3}{2} N_A$ for H_2 and D_2, which cannot be reached for other gases since liquefaction of the gas takes place. On the contrary, the heat capacity increases with rising temperature, but the theoretical value of the heat capacity $C_V = \frac{7}{2} N_A$ is not reached, since dissociation of gas molecules into atoms begins.

The reason for the discrepancy between experiment and the predictions of classical theory will be considered in Secs. 46 and 47, showing that the contradiction vanishes in the theory that accounts for energy quantization.

The Boltzmann distribution can be used to determine the probability density for any generalized coordinate and any generalized momentum. These distributions acquire a very simple form when we introduce the so-called *normal coordinates* in which, as is known (see, for instance, [6]), the quadratic formulae for the kinetic and potential energies reduce simultaneously to the diagonal form:

$$\varepsilon = a_i p_i^2 + b_r q_r^2.$$

Integrating the Boltzmann distribution over all momenta and coordinates, except those of interest to us, we obtain

$$dW(p_i) = \frac{e^{-a_i p_i^2/T} dp_i}{\int e^{-a_i p_i^2/T} dp_i}, \quad dW(q_r) = \frac{e^{-b_r q_r^2/T} dq_r}{\int e^{-b_r q_r^2/T} dq_r},$$

i.e. the Gaussian distribution for each normal coordinate and for each generalized momentum.

The equipartition theorem can be formulated not for the energy of one mole of a gas, but the average energy of a molecule. Each rotational and translational degree of freedom contribute $\frac{T}{2}$ to the average molecular energy, and the contribution of each vibrational degree of freedom amounts to T. The advantage of this statement of the equipartition theorem consists in that it is applicable not only to ideal classical gases consisting of molecules, but also to individual, noninteracting with each other objects with an intricate internal structure, considering each such object as a molecule. This technique will be applied, for instance, in Sec. 52 for a classical treatment of light radiation, and it will be used in Sec. 53 for heat capacity of crystals in the classical approximation.

Problem

Find the classical value of C_V for gases: CO_2 (linear molecule), H_2O (non-linear molecule), NH_3.

44. The Maxwell-Boltzmann Gas with Two Energy Levels

Let us consider a system of non-interacting particles, obeying the Maxwell-Boltzmann distribution and having two energy levels $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$ with degeneracies g_0 and g_1 respectively. An example of such a system, for instance, is the totality of N particles with magnetic moments μ fixed at the sites of a crystal lattice. If the spin of these particles is $s = 1/2$, then the energy of each such particle placed in a magnetic field with an intensity H acquires two values: $-\mu H$, if the magnetic moment is parallel to the field, and μH, if the magnetic moment is antiparallel to the field. Of a considerably greater interest is the fact that many physical systems with quantized energies at low temperatures are similar in their thermodynamic properties to a two-level system. Such similarity appears when at sufficiently low temperatures the number of particles on all levels, beginning from the third level and higher, is small compared to the number of particles occupying the first two levels. Situations of this kind will be encountered below in Secs. 46, 50, 51.

Write the expressions for the level occupation numbers:

$$N_0 = g_0 e^{\mu/T}, \quad N_1 = g_1 e^{(\mu-\varepsilon)/T}. \tag{44.1}$$

Finding the chemical potential from the condition $N_0 + N_1 = N$,

$$e^{\mu/T} = \frac{N}{g_0 + g_1 e^{-\varepsilon/T}},$$

we obtain

$$N_0 = N \frac{g_0}{g_0 + g_1 e^{-\varepsilon/T}}, \tag{44.2}$$

$$N_1 = N \frac{g_1 e^{-\varepsilon/T}}{g_0 + g_1 e^{-\varepsilon/T}}. \tag{44.3}$$

The internal energy of the system is expressed by

$$U = N_1 \varepsilon = \frac{N\varepsilon g_1 e^{-\varepsilon/T}}{g_0 + g_1 e^{-\varepsilon/T}} = \frac{N\varepsilon g_1}{g_0 e^{\varepsilon/T} + g_1} \tag{44.4}$$

and, differentiating energy U with respect to temperature, we get

$$C = \frac{N g_0 g_1 (\varepsilon/T)^2 e^{\varepsilon/T}}{(g_0 e^{\varepsilon/T} + g_1)^2}. \tag{44.5}$$

The heat capacity of the system diminishes as $T \to 0$ in proportion to $e^{-\varepsilon/T}$ and at $T \to \infty$, as T^{-2} and, consequently, the heat capacity reaches a maximum value at a certain temperature T_{max} (Fig. 62). Let us find the temperature corresponding to the maximum heat capacity, T_{max}, and the width of the maximum, assuming the ratio of the degeneracies of the excited and ground states, g_1/g_0, to be exponentially large, $\ln(g_1/g_0) \gg 1$.

Differentiating Eq. (44.5) and equating the derivative $\frac{dC}{dT}$ to zero, we find for T_{max} the specifying equation

$$\frac{\varepsilon}{T_{max}} = \ln \frac{g_1}{g_0} + \ln \frac{\varepsilon/T_{max}+2}{\varepsilon/T_{max}-2}, \tag{44.6}$$

for which at $\ln(g_1/g_0) \gg 1$ the approximate solution is

$$T_{max} = \frac{\varepsilon}{\ln(g_1/g_0)}. \tag{44.7}$$

Substituting into Eq. (44.5) the value of T_{max} from Eq. (44.7), we find the maximum heat capacity

$$C_{max} = \frac{1}{4} N \ln^2(g_1/g_0), \tag{44.8}$$

and the relationship $C_{max}\Delta T \approx \Delta U \cong N\varepsilon$ permits to estimate the width of the maximum:

$$\Delta T \propto \frac{4\varepsilon}{\ln^2(g_1/g_0)}.$$

The physical interpretation of the obtained results is obvious. For a two-level system there exists a range of temperatures, close to T_{max}, within which an intensive transition of particles from the ground level to the excited takes place. Below this temperature the main fraction of particles occupies the level $\varepsilon_0 = 0$ and above this temperature the distribution of particles over energy levels approaches the uniform one, $N_1/N_0 \approx g_1/g_0$. If $\ln(g_1/g_0) \gg 1$, the order of magnitude of the temperature T_{max}, at which a considerable fraction of particles has already passed to the level $\varepsilon_1 = \varepsilon$, is $\ln(g_1/g_0)$ times smaller than ε, and the temperature interval within which this transition occurs is still $\ln^2(g_1/g_0)$ times smaller.

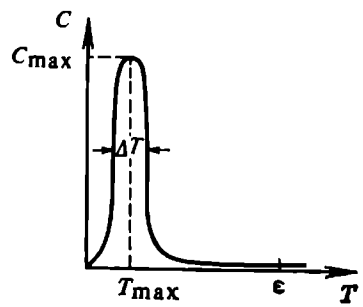


FIG. 62

It follows from the foregoing that in a two-level system the larger the ratio of the degeneracies of the excited and ground levels, the lower the temperatures and the narrower the temperature interval within which the transition to the excited state occurs. These regularities remain quantitatively valid for systems with more than two energy levels, if the third level is separated from the second by a sufficiently large energy interval, so that at low temperatures a considerable fraction of molecules occupy the first two levels.

Problem

Find T_{max}, C_{max} and ΔT for the limiting case $g_1/g_0 \ll 1$ (contrary to that considered in this section).

Answer. $T_{max} = \frac{\varepsilon}{2}$, $C_{max} \approx \frac{4}{e^2} \frac{g_1}{g_0} N$, $\Delta T = \frac{e^2}{4} \varepsilon$.

45. Quantization of Translational Motion

Considering in Sec. 40 a monoatomic ideal gas, we have found the thermodynamic functions of the gas, assuming it to be nondegenerate and neglecting energy quantization. In this section, again assuming the gas to be nondegenerate, we take into account the energy quantization of particles moving in a vessel of confined volume.

The Maxwell-Boltzmann statistics with quantized energy permits the introduction of the concept of the sum over states (also referred to as the *partition function*) Z, identical with the concept of the integral of states.

Eliminate from the expressions

$$N = \sum_i g_i e^{(\mu - \varepsilon_i)/T}, \quad U = \sum_i g_i \varepsilon_i e^{(\mu - \varepsilon_i)/T}$$

the chemical potential to obtain

$$U = N \frac{\sum_i g_i \varepsilon_i e^{-\varepsilon_i/T}}{\sum_i g_i e^{-\varepsilon_i/T}}.$$

Introducing now the partition function

$$Z = \sum_i g_i e^{-\varepsilon_i/T},$$

we can rewrite the above formula to read

$$U = NT^2 \frac{\partial}{\partial T} (\ln Z).$$

The Ω-potential of gas is found by formula (38.17):

$$\Omega = -Te^{\mu/T} Z.$$

(We consider it useful to recall that in all formulae of this section the summation sign $\sum_i$ implies summation not over the arbitrarily introduced energy "boxes", but over the quantized energy levels, and therefore the numbers g_i denote the level degeneracies.)

Let us turn now to the problem on the quantization of energy of a particle in translational motion in a vessel of confined volume. For the sake of simplicity the vessel is assumed to be a cube with an edge L. As is known from quantum mechanics (see, for instance [7]) the permissible values of the energy of a particle confined in a box with impermeable walls are given by the formula

$$\varepsilon(n_1, n_2, n_3) = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2),$$

and the wave function of states with a definite energy is

$$\psi(n_1, n_2, n_3) = C(n_1, n_2, n_3) \sin\left(\frac{n_1\pi x}{L}\right) \sin\left(\frac{n_2\pi y}{L}\right) \sin\left(\frac{n_3\pi z}{L}\right),$$

where n_1, n_2, n_3 are integers assuming the values of 1, 2, 3, ... The values $n_i = 0$ are inadmissible, since in this case the wave function becomes zero identically; neither should negative values of n_i be assumed to be independent, since upon a change in the sign of n_i the wave function is only multiplied by —1.

For each set of numbers n_1, n_2, n_3 there exists one particle state; therefore, the partition function must involve summation over n_1, n_2, n_3 independently over all values from 1 to ∞, and the degeneracy $g(n_1, n_2, n_3)$ must be assumed equal unity. The energy levels $\varepsilon(n_1, n_2, n_3)$ are assumed then to be degenerate with a degeneracy equal to the number of solutions of the equation $n_1^2 + n_2^2 + n_3^2 = n$ expressed in integers; however, this degeneracy is accounted for automatically due to the fact that summation is performed not over the energy levels, but over all values of n_1, n_2, n_3.

The partition function is expressed by

$$Z = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \exp\left[-\frac{h^2}{8L^2mT}(n_1^2 + n_2^2 + n_3^2)\right] = \left(\sum_{n=1}^{\infty} e^{-(\pi T_t/T)n^2}\right)^3,$$

where the *characteristic temperature for translational motion*, T_t, is specified by the formula

$$T_t = \frac{h^2}{8\pi mL^2}. \qquad (45.1)$$

Let us introduce the function $\theta(x)$, defined by the formula

$$\theta(x) = \sum_{n=-\infty}^{\infty} e^{-\pi n^2 x}. \tag{45.2}$$

The definition of the function $\theta(x)$ infers its asymptotic representation at large values of the argument, $x \gg 1$:

$$\theta(x) = 1 + 2e^{-\pi x} + 2e^{-4\pi x} + \ldots .$$

We shall also need the asymptotic representation of the function $\theta(x)$ at small values of the argument, $x \ll 1$, and it is rather difficult to find it from formula (45.2). It can, however, be found using the functional equation for the function $\theta(x)$ [see Mathematical Appendix, formula (VI.5)]:

$$\theta(x) = \frac{1}{\sqrt{x}}\,\theta\left(\frac{1}{x}\right).$$

The formula for the partition function can be presented with the aid of the function $\theta(x)$ in the form

$$Z = \frac{1}{8}\left[\theta\left(\frac{T_t}{T}\right) - 1\right]^3,$$

and the functional equation for $\theta(x)$ permits representation of the partition function in the form

$$Z = \frac{1}{8}\left(\frac{T}{T_t}\right)^{3/2}\left[\theta\left(\frac{T}{T_t}\right) - \sqrt{\frac{T_t}{T}}\right]^3.$$

It should be noted now that according to (45.1) the characteristic temperature T_t is inversely proportional to L^2 or $V^{2/3}$. Therefore at any finite temperature the ratio $T_t/T \ll 1$ and all higher powers of T_t/T must be successively dropped at the thermodynamic limit, and the function $\theta(T/T_t)$ should be replaced by unity. Then, according to the latter formula,

$$Z = \frac{1}{8}\left(\frac{T}{T_t}\right)^{3/2} = V\frac{(2\pi mT)^{3/2}}{h^3}. \tag{45.3}$$

Since at high temperatures it is admissible to ignore energy quantization, expression (45.3) must coincide with the integral of states divided by the cell volume a, since when passing to integration g_l turns into $d\Gamma/a$, and not into $d\Gamma$. Comparing (45.3) with Z_{cl}/a from formula (40.4), we find $a = h^3$. The attention of the reader is drawn to the fact that in this section we have solved for the first time the problem formulated in Sec. 33, i.e. we have found the volume of an elementary cell, a, for a six-dimensional μ-space of three translational degrees of freedom. This volume turned out to be equal to h^3. It will be shown in the following section and also in Sec. 48 that similar results can be obtained when considering rotational and

vibrational degrees of freedom: each degree of freedom introduces into the cell volume a the factor h. It should be emphasized that this result is obtained within the framework of the Maxwell-Boltzmann distribution for a nondegenerate gas, but with account taken of energy quantization. It will be demonstrated in Ch. V that the cell volume a can be found experimentally and with no account taken of energy quantization, but for the objects obeying the Bose-Einstein and Fermi-Dirac distributions, namely, for highly degenerate gases. It should be noted in concluding this section that since the characteristic temperature T_t of translational motion must be considered equal to zero, quantization of translational motion does not change the formulae for the internal energy, heat capacity, entropy and chemical potential derived in Sec. 40.

46. Diatomic Gas. Rotational Degrees of Freedom

Calculating in Sec. 43 the energy and heat capacity of a polyatomic ideal gas in the frames of classical approximation, we proved the energy (and also heat capacity) equipartition theorem. The result obtained was presented in the form

$$U = l\frac{N_A T}{2}, \quad C_V = l\frac{N_A}{2}, \quad C_P = (l+2)\frac{N_A}{2}, \quad \gamma = \frac{C_P}{C_V} = \frac{l+2}{l},$$

where l is the number of translational and rotational degrees of freedom of a molecule plus the doubled number of vibrational degrees of freedom. This result was shown in the same section to be in disagreement with experimental data. The heat capacity of diatomic gases, for instance, instead of being equal to $\frac{7}{2} N_A$, changes with temperature, following a step curve, shown schematically in Fig. 63 (the dotted section of the curve is valid only for H_2 and D_2). In addition to this discrepancy with experimental results, the equipartition law contradicts the Nernst theorem, according to which the heat capacity must tend to zero at $T \to 0$.

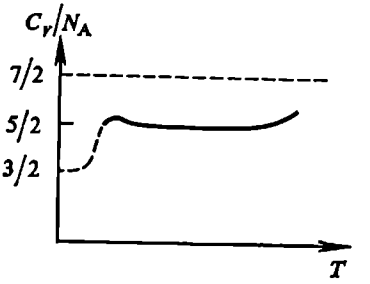


FIG. 63

The two contradictions can be removed if we make use of the approximation mentioned in Sec. 39 and, assuming the gas to be nondegenerate and using the Boltzmann distribution, take account for the quantization of energy levels. In this case all kinds of molecular energy are quantized: translational, rotational and vibrational. The minimum portions (quanta) of these kinds of energy, how-

ever, sharply differ in magnitude. By the orders of magnitude the quanta of translational energy $\Delta\varepsilon_t$, rotational $\Delta\varepsilon_r$, vibrational $\Delta\varepsilon_v$, electronic $\Delta\varepsilon_e$ and nuclear energy $\Delta\varepsilon_n$ are related as follows:

$$\Delta\varepsilon_t \ll \Delta\varepsilon_r \ll \Delta\varepsilon_v \ll \Delta\varepsilon_e \ll \Delta\varepsilon_n. \quad (46.1)$$

It follows that the characteristic temperature T_t for the translational, T_r for the rotational, T_v for the vibrational, T_e for the electronic and T_n for the nuclear motions also satisfy a similar inequality:

$$T_t \ll T_r \ll T_v \ll T_e \ll T_n. \quad (46.2)$$

Studying the quantization of translational motion in the preceding section, we learned that the characteristic temperatures for translational motion, T_t, were extremely low and, therefore, $T_t \ll T$ and $\Delta\varepsilon_t \ll T$ at any temperatures attainable. This means that the translational motion makes completely a classical contribution to the internal energy of a gas $\left(\frac{3}{2} N_A T\right)$ and to its heat capacity $\left(\frac{3}{2} N_A\right)$. It should be recalled that the gas degeneracy temperature is considerably higher than the characteristic temperature T_t and at $T < T_t$ the gas does not obey the Maxwell-Boltzmann distribution at all, not to mention the fact that at such temperatures all gases liquefy or solidify.

Let us consider now qualitatively the behaviour of the other degrees of freedom of a diatomic gas.

So long as the molecular energy, which is proportional to T, is smaller than T_r ($T < \Delta\varepsilon_r$), the rotational and the more so the vibrational degrees of freedom are not excited during collisions and the gas behaves as a monoatomic gas. At higher temperatures $\Delta\varepsilon_r < T < \Delta\varepsilon_v$, the rotational degrees of freedom become excited during collisions, but oscillations remain frozen, and the heat capacity $C_V = \frac{5}{2} N_A$. Finally, at $T \gtrsim T_v$ vibrations of atoms initiate, but at the same time quasi-elastic molecular bonds are ruptured, i.e. molecules dissociate into atoms and, therefore, oscillations never make full classical contribution to the energy and heat capacity, $N_A T$ and N_A, per each degree of freedom. The electronic degrees of freedom (electron excitation and atomic ionization) "come into the play" at still higher temperatures, $T_e \sim (10^4$ to $10^5)$ K, when the gas becomes plasma. Finally, excitation of the intranuclear degrees of freedom (thermonuclear reactions) takes place at temperatures of the order of $T_n \sim (10^7$ to $10^8)$ K and above. Such is the rough explanation of the step curve shown in Fig. 63.

Let us turn now to a more detailed examination, beginning with the rotational degrees of freedom and limiting ourselves in this section to the consideration of molecules consisting of two different

atoms (CO, HCl, etc.). Gases whose molecules consist of two similar atoms will be treated in the following section.

Quantum mechanics proves that the energy of a rotating particle with two rotational degrees of freedom, of a three-dimensional rotator, is specified by formula

$$\varepsilon_r = \frac{h^2}{8\pi^2 J} l(l+1), \tag{46.3}$$

where l = rotational quantum number, $l = 0, 1, 2, \ldots$;
J = moment of inertia of particle.

In the case under consideration, $J = ma^2$, where $m = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the atoms forming the molecule, and a is the interatomic distance assumed here to be constant, ignoring the effect of atomic oscillation on the rotational motion.

Energy levels [formula (46.3)] are degenerate and the degeneracy is equal to $2l + 1$, since at a given value of the square angular momentum, $M^2 = \frac{h^2}{4\pi^2 J} l(l+1)$, its projection on a certain direction may assume all values from $-l\frac{h}{2\pi}$ to $+l\frac{h}{2\pi}$.

Thus, the partition function

$$Z = \sum_{l=0}^{\infty} (2l+1) \exp\left[-\frac{h^2 l(l+1)}{8\pi^2 JT}\right].$$

Introducing the *characteristic rotational temperature*

$$T_r = \frac{h^2}{8\pi^2 J}, \tag{46.4}$$

let us rewrite the expression for Z in the form

$$Z = \sum_{l=0}^{\infty} (2l+1) \exp\left[-\frac{T_r l(l+1)}{T}\right]. \tag{46.5}$$

Series (46.5) is not found in the finite form, and we shall consider two limiting cases.

High Temperatures $T \gg T_r$. The distances between the rotational energy levels are then small compared to the average energy,

$$\frac{\varepsilon\Delta_r}{T} \propto \frac{T_r}{T} \ll 1, \tag{46.6}$$

and energy quantization can be ignored, assuming the rotational energy to be a continuously varying quantity. Therefore in this approximation the partition function must coincide with the integral of states divided by the phase volume of a cell for rotational degrees of freedom, $\frac{Z_{cl}}{a}$ (cf. Sec. 39).

In classical mechanics rotational energy is expressed by the formula

$$\varepsilon_r = \frac{J}{2}[\dot{\theta}^2 + \sin^2\theta\dot{\varphi}^2],$$

where θ and φ are the angles determining the direction of the molecular axis (Fig. 64) chosen as generalized coordinates. The respective generalized momenta are equal to

$$p_\theta = \frac{\partial\varepsilon_r}{\partial\dot{\theta}} = J\dot{\theta}, \quad p_\varphi = \frac{\partial\varepsilon_r}{\partial\dot{\varphi}} = J\sin^2\theta\dot{\varphi}.$$

Energy is expressed as a function of generalized coordinates and momenta by the formula

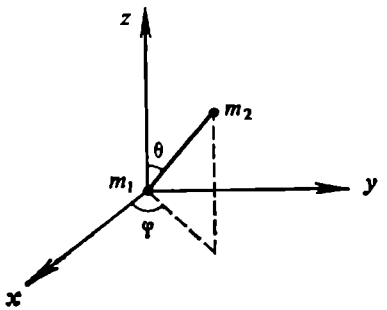


FIG. 64

$$\varepsilon_r = \frac{p_\theta^2 + p_\varphi^2/\sin^2\theta}{2J}. \quad (46.7)$$

Consequently, the integral of states will have the form

$$Z_{cl} = \int_0^\pi d\theta \int_0^{2\pi} d\varphi \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\varphi \times \exp\left[-\frac{p_\theta^2 + p_\varphi^2/\sin^2\theta}{2JT}\right].$$

Integrating first over φ, p_θ and p_φ then over θ, we obtain

$$Z_{cl} = 8\pi^2 JT. \quad (46.8)$$

On the other hand, in the limiting case under consideration, the expression for the partition function can be replaced by the integral over l, since at $T_r/T \ll 1$ the summed up expression

$$(2l+1)\,e^{-T_r l(l+1)/T}$$

changes slightly as l changes by unity.

Let us transform Eq. (46.5) by means of Euler's summation formula (see, for example, [8]) that can be here presented in the form

$$\sum_{l=0}^{\infty} f(l) = \int_0^\infty f(l)\,dl + \frac{1}{2}[f(0) + f(\infty)] + \frac{1}{12}[f'(\infty) - f'(0)] - \ldots \quad (46.9)$$

(the function $f(l)$ is assumed to be integrable on the interval $(0, \infty)$ and all its derivatives are considered to be finite at $l \to 0$ and $l \to \infty$).

The series on the right-hand side of formula (46.9) often turns out to be divergent; its first terms, however, usually give for a slowly varying $f(l)$ a good approximation for the sum of the series on the left-hand side of formula (46.9).

In the case under consideration, substituting $f(l) = (2l+1) \times \times e^{-T_r l(l+1)/T}$, we obtain

$$Z_r = \int_0^\infty e^{-T_r l(l+1)} (2l+1)\, dl + \frac{1}{2} + \frac{1}{12}\frac{T_r}{T} + O\left[\left(\frac{T_r}{T}\right)^3\right]. \qquad (46.10)$$

The integral in expression (46.10) can be evaluated, and we obtain

$$Z_r \approx \frac{T}{T_r}\left[1 + \frac{1}{3}\frac{T_r}{T} + \frac{1}{15}\left(\frac{T_r}{T}\right)^2\right]. \qquad (46.11)$$

whence, expanding $\ln\left[1 + \frac{1}{3}\frac{T_r}{T} + \frac{1}{15}\left(\frac{T_r}{T}\right)^2\right]$ into a series, we find the expression for the internal energy:

$$U_r = NT^2 \frac{\partial}{\partial T}(\ln Z_r) = NT\left[1 - \frac{1}{3}\frac{T_r}{T} - \frac{1}{45}\left(\frac{T_r}{T}\right)^2\right]. \qquad (46.12)$$

For the rotational heat capacity we have

$$C_r = \frac{\partial U_r}{\partial T} = N\left[1 + \frac{1}{45}\left(\frac{T_r}{T}\right)^2\right] \approx N. \qquad (46.13)$$

Formula (46.13) shows that at $T \gg T_r$ the heat capacity C_r approaches its classical limit N from above and, consequently, has a maximum value at a certain temperature T_{max}. Numerical integration yields the value $T_{max} \approx 0.81 T_r$, and the relative value of the maximum of C_r (compared to the classical limit N) amounts to 1.1. The origin of the peak on the curve C_r becomes clear if we recall the results obtained in Sec. 44.

At temperatures $T \lesssim T_r$ the relative number of particles occupying the level $l = 2$ and higher levels is rather small, and it can be estimated by the formula

$$\frac{N_l}{N} = \frac{(2l+1)\, e^{-T_r l(l+1)/T}}{\sum_{l=0}^{\infty} (2l+1)\, e^{-T_r l(l+1)/T}},$$

and at $T \approx T_r$, $l = 2$ amounts to about 0.9×10^{-2}. It follows that at $T \lesssim T_r$ rotational degrees of freedom of a molecule behave like a two-level system. The ratio of the degeneracies for the second ($l = 1$) and the first ($l = 0$) levels equals 3, and though the ratio is not very large, it is sufficient for the maximum to appear on the curve representing heat capacity as a function of temperature.

Equating the limiting value of the partition function (46.11), $Z = T/T_r$, to the quantity Z_{cl}/a_r (a_r is the phase volume of a cell

for rotational degrees of freedom), we find that

$$a_r = h^2. \tag{46.14}$$

Low Temperatures $T \ll T_r$. In this limiting case the terms in the partition function (46.5) decrease rapidly with increasing l, and it is sufficient to take the first two terms of the series:

$$Z_r = 1 + 3e^{-2T_r/T}.$$

Then, we have

$$U_r = NT^2 \frac{\partial}{\partial T}\left[\ln\left(1 + 3e^{-2T_r/T}\right)\right] \approx 6NT_r e^{-2T_r/T}, \tag{46.15}$$

$$C_r = 12N\left(\frac{T_r}{T}\right)^2 e^{-2T_r/T}. \tag{46.16}$$

According to the Nernst theorem, C_r and U_r tend to zero as $T \to 0$. Thus, the rotational degrees of freedom are fully excited and contribute respectively $\frac{N_A T}{2}$ and $\frac{N_A}{2}$ to the internal energy and heat capacity at $T \gg T_r$, and "freeze out" at $T \ll T_r$.

It should be noted that the rotational characteristic temperatures are inversely proportional to the moment of inertia J and, therefore, the maximum values of T_r are associated with gases whose molecules are composed of light atoms and are of a small size. The order of T_r for most gases is (1 to 10) K, i.e. the characteristic temperature is lower than the condensation temperature and it proves impossible to observe the "freezing out" of rotational degrees of freedom for such gases.

The "freezing out" of rotational degrees of freedom, associated with energy quantization, can be observed only for the DH gas whose rotational characteristic temperature is about 64 K, which is higher than the liquefaction temperature of this gas.

Concluding this section, let us calculate the chemical potential of rotational degrees of freedom, the expression for which will be used in Secs. 50 and 51.

By the formula $N = \sum_i g_i e^{(\mu - \varepsilon_i)/T}$ we have

$$\mu = T \ln (N/Z).$$

Substituting Z in the form of a product of the partition functions of the translational, rotational and vibrational degrees of freedom, $Z = Z_t Z_r Z_v$ (it should be recalled that the relation between oscillation and rotation is ignored in this section), we obtain

$$\mu_r = -T \ln Z_r$$

[the term $T \ln N$ is included in μ_t in formula (40.5)].

Substituting the value of Z_r in the two limiting cases of $T \gg T_r$ and $T \ll T_r$, we find at $T \gg T_r$

$$\mu_r = -T \ln T + T \ln T_r = -T \ln T + T \ln \left(\frac{h^2}{8\pi^2 J} \right) \quad (46.17)$$

and at $T \ll T_r$

$$\mu_r = -T \ln (1 + 3e^{-2T_r/T}) \approx -3Te^{-2T_r/T}. \quad (46.18)$$

47. Molecules Consisting of Identical Atoms. Ortho- and Paramodifications

If a gas molecule consists of two identical atoms, a new symmetry element appears in it: the state of the molecule does not change upon atomic permutation or upon reflection in a plane of symmetry. This leads to some changes in the thermodynamic functions of the gas.

These changes can be readily found in the case where the gas temperature is high compared to the characteristic rotational temperature, $T \gg T_r$, so that energy quantization can be neglected. The rotational integral of states then must be divided by two to account for the equivalency of the states differing from one another by the atomic permutations. The expressions for U_r and C_r, remain unchanged and the additional term $T \ln 2$ appears in expression (46.17) for the chemical potential.

The changes in gas thermodynamics appearing in the case when $T \ll T_r$ are of a particular interest. We assume, however, the gas to remain of the Maxwell-Boltzmann kind, i.e. its temperature is considerably higher than the degeneracy temperature. As has been already mentioned, such a situation can occur only for molecular hydrogen H_2 and deuterium D_2. Only these two gases will be dealt with in the following treatment. Let us first examine in greater detail the case involving hydrogen.

A hydrogen molecule is formed by two protons having spins $s = 1/2$. The total spin S^* can, therefore, acquire the values of $S^* = 0, 1$ with degeneracies $g_{S^*} = 2S^* + 1$, equal respectively to $g_{S^*} = 1, 3$. Modifications with a greater statistical weight are called *orthomodifications* (in the case of hydrogen orthomodifications are molecules with parallel proton spins for which $S^* = 1$ and the statistical weight equals 3/4), while modifications with a smaller statistical weight are referred to as *paramodifications* (for hydrogen these are molecules with antiparallel spins for which $S^* = 0$ and the statistical weight equals 1/4). In quantum mechanics use is made of the so-called adiabatic approximation in which, due to the large magnitude of the ratio M/m (M is the mass of the nucleus and m is the mass of the electron), the wave function of a molecule is expressed by the product of the wave function of nuclei and the wave function of electrons [7].

In the nuclear centre-of-mass system the wave function of nuclei is the product of the coordinate function $R(r, \theta, \varphi)$ and the spin wave function $\chi(\sigma_1, \sigma_2)$, where r, θ, φ, are the spherical coordinates of a "particle" having a reduced mass $M/2$ in the centre-of-mass system, and σ_1, σ_2 are nuclear spin variables (spin projections on the direction of the moment quantization axis, $\sigma_i = \pm 1/2$). As is known from quantum mechanics [7], the symmetry of a coordinate wave function with respect to nuclear permutation, i.e. inversion of the radius-vector r, is determined by the rotational quantum number l, and the parity of this function $P_r = (-1)^l$, while the parity of the spin function is specified by the expression $(-1)^{S^*+1}$. Since the total wave function of a system of protons (Fermi-Dirac particles) must be antisymmetric, then for orthohydrogen the rotational quantum number l can assume only odd values 1, 3, 5, . . ., and for parahydrogen, only even values 0, 2, 4, ... For this reason the partition function for hydrogen in thermodynamic equilibrium is expressed by

$$Z_r = \frac{3}{4} Z_o + \frac{1}{4} Z_p = \frac{3}{4} \sum_{l=1, 3, \ldots} (2l+1)\, e^{-T_r l(l+1)/T} + \frac{1}{4} \sum_{l=0, 2, \ldots} (2l+1)\, e^{-T_r l(l+1)/T}, \quad (47.1)$$

whence all thermodynamic functions of the gas can be found. We can find, in particular, the ratio of the number of molecules of orthohydrogen, N_o, to the number of molecules of parahydrogen, N_p, in thermodynamic equilibrium:

$$\frac{N_o}{N_p} = 3 \frac{Z_o}{Z_p}. \quad (47.2)$$

At temperatures high compared to T_r, the two partition functions, Z_o and Z_p, can be approximately replaced by integrals, and as $T \to \infty$ they will tend to the limit $\frac{1}{2} Z_{cl} = 4\pi^2 JT$ [see Eq. (46.8)] with the ratio N_o/N_p tending to 3, in such a high-temperature gas $N_o = \frac{3}{4} N$ and $N_p = \frac{1}{4} N$. On the contrary, at $T \ll T_r$, we have $Z_o \approx 3 \exp[-2T_r/T]$ and $Z_p \approx 1$, and the ratio N_o/N_p becomes rather small: in a sufficiently large time interval practically all molecules pass to the ground level $l = 0$ which corresponds to a paramodification.

It should be noted that for pure ortho- and paramodifications of hydrogen the curves presenting heat capacity as a function of temperature behave in a different manner. The curve $C_p(T)$ has a maximum and there is no maximum on the curve $C_o(T)$ (Fig. 65), which is due to the fact that the ratios of degeneracies of the normal and

excited states for ortho- and parahydrogen are different. For parahydrogen ($l = 0, 2$) this ratio $g_2/g_0 = 5$ is sufficiently high for a "two-level" maximum to appear. For orthohydrogen ($l = 1, 3$) this ratio is $g_3/g_1 = 7/3$ and the "two-level" effect is small. The curve presenting the heat capacity of a mixture of para- and orthomodifications as a function of temperature has, however, a maximum (dotted line in Fig. 65).

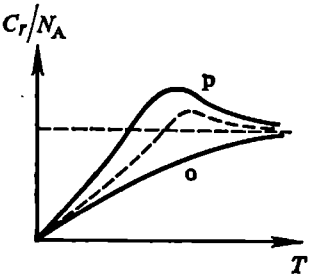


FIG. 65

It should be emphasized, however, that the transitions between the energy levels of ortho- and paramodifications proceed at a rather low rate, especially at low temperatures, which can be explained by the fact that the spin of one of the protons can be "turned over" only by magnetic interactions that are rather weak in ordinary conditions. For this reason, at not very high temperatures and in the absence of special catalysts, hydrogen behaves over rather long periods of time (days or even months) as a mixture of components not changing into one another. The thermodynamic functions of such a metastable state must be calculated, therefore, as for a mixture.

Let us consider by way of illustration the following problem. One mole of hydrogen, having initial temperature T_0 high compared to T_r, was rapidly cooled to temperature $T \ll T_r$ and kept for a long time in a constant-volume thermostat, until the gas passes into a completely equilibrium state.

Let us find the change in the external energy, the change in entropy and in the quantity of heat liberated during the cooling process. Since the initial mixture consisted of $\frac{3}{4} N_A$ molecules of orthohydrogen and $\frac{1}{4} N_A$ molecules of parahydrogen (in the course of rapid cooling from temperature $T_0 \gg T_r$ to $T \ll T_r$ this proportion had not changed), the initial rotational chemical potential must be calculated for the mixture of the two gases:

$$\mu_1 = \frac{3}{4} \mu_o + \frac{1}{4} \mu_p. \tag{47.3}$$

Since the number of orthohydrogen and parahydrogen molecules changes as thermodynamic equilibrium sets in, the term $T \ln N$ must be included in the rotational and not the translational chemical potential. According to formula $\mu_r = -T \ln \left(\frac{Z_r}{N}\right)$, for the poten-

tials μ_o and μ_p we have

$$\mu_o = -T \ln \left(\frac{3/4\, Z_o}{3/4\, N} \right) = T \ln \frac{N}{Z_o},$$

$$\mu_p = -T \ln \left(\frac{1/4\, Z_p}{1/4\, N} \right) = T \ln \frac{N}{Z_p},$$

whence we find that

$$\mu_i = T \left[\ln N - \frac{3}{4} \ln Z_o - \frac{1}{4} \ln Z_p \right]. \tag{47.4}$$

In the final state $N_p \approx N$, $N_o \ll N$ and

$$\mu_f = T \left[\ln N - \ln \left(\frac{1}{4} Z_p \right) \right].$$

The change in the chemical potential is expressed by

$$\Delta\mu = \mu_f - \mu_i = T \left(\frac{3}{4} \ln Z_o - \frac{3}{4} \ln Z_p + \ln 4 \right).$$

Substituting at $T \ll T_r$ the approximate values

$$Z_o \approx 3e^{-2T_r/T}, \quad Z_p \approx 1$$

(in Z_p we drop the exponentially small term $5e^{-6T_r/T}$), we finally obtain

$$\Delta\mu = T \left(\frac{3}{4} \ln 3 + \ln 4 - \frac{3}{2} \frac{T_r}{T} \right),$$

whence the change in molar entropy $\widetilde{S}$ is

$$\Delta\widetilde{S} = -N_A \frac{\partial \Delta\mu}{\partial T} = -\frac{N_A}{4} \ln (3^3 \cdot 4^4). \tag{47.5}$$

Thus, as equilibrium sets in, entropy diminishes. This, naturally, is not in contradiction to the law of entropy increase for irreversible processes, since here the gas is not heat-insulated but placed in a thermostat where it transfers heat and, consequently, entropy to the thermostat (this will be shown below). From the viewpoint of statistical physics the decrease in entropy in the process under consideration is accounted for by the gas passing from a "more degenerate" to a "less degenerate" state.

Actually, in the initial state, firstly, there exist $\frac{N!}{N_o!\, N_p!}$ ways of subdividing the molecules into groups of orthomolecules and paramolecules and, secondly, the state of each of the orthomolecules is nine-fold degenerate (at $T \ll T_r$ practically all orthomolecules are in a state in which $l = 1$ and there exists a three-fold spin degeneracy, $S^* = 1$, and a three-fold degeneracy in orbital momentum). Therefore the total number of methods of realizing the initial state

is equal to

$$W_1 = \frac{N_A!\, 9^{3N_A/4}}{(3/4\,N_A)!\,(1/4\,N_A)!} = 4^{N_A} 3^{3N_A/4}.$$

[Stirling's formula $N! = (N/e)^N$ is used here]. In contrast to this, the final state is determined uniquely. All of the N_A molecules are in a parastate with $S^* = 0$, $l = 0$, and $W_f = 1$. Hence, by the Boltzmann formula $S = \ln W$, we obtain again the same result: $\Delta S = \ln \frac{W_f}{W_1} = -\frac{N_A}{4} \ln (3^3 \times 4^4)$. The change in the internal energy of the gas can be calculated thermodynamically, for instance, by the formula $F = -T \ln (Ze/N) = U - TS$.

Preference is given, however, to elementary calculations based on the assumption that in the process under consideration $\frac{3}{4} N_A$ molecules pass from the level $l = 1$ to the level $l = 0$, ignoring the small number of particles occupying other levels. The result is

$$\Delta U_r = \frac{3}{4} N_A [\varepsilon_r|_{l=0} - \varepsilon_r|_{l=1}] = -\frac{3}{4} N_A \frac{h^2}{8\pi^2 J} \cdot 2 = -\frac{3}{2} N_A T_r. \quad (47.6)$$

Since the process works isochorically and the gas performs no work, $\Delta Q = \Delta U_r$ and $\Delta Q = -\frac{3}{2} N_A T_r$. It should be noted that because the process is non-equilibrium the quantity of heat cannot, of course, be calculated by the change in entropy, since the formula $\Delta Q = T\,\Delta S$ is invalid.

Similar results can also be obtained for molecular deuterium D_2, with the following changes. Since each deuteron has a spin $s = 1$ and is a boson, the total spin can assume the values $S^* = 0, 1, 2$ with statistical weights $\frac{1}{9}, \frac{3}{9}, \frac{5}{9}$ respectively. The spin wave function is antisymmetric in states with $S^* = 0$ and $S^* = 2$, and, consequently, the coordinate wave function must also be antisymmetric (in a boson system the total wave function must be symmetric). Combining the two cases, the name orthodeuterium is given to a gas whose molecules have an even spin. The statistical weights of these states are equal to $\frac{1}{9} + \frac{5}{9} = \frac{2}{3}$ and, just as in the case of orthohydrogen, they combine with the odd values of the rotational quantum number $l = 1, 3, \ldots$.

The states with $S^* = 1$ form the paradeuterium having a statistical weight $\frac{1}{3}$ and even values of l ($l = 0, 2, \ldots$).

The remaining results should be calculated by the reader.

Problem

Find the change in energy, entropy and in the quantity of heat when one mole of D_2 passes to an equilibrium state at $T =$ $=$ const ($T \ll T_r$).

Answer. $\Delta S = -\frac{5}{3} N_A \ln 3$, $\Delta Q = \frac{2}{3} N_A T_r$.

48. Vibrational Degrees of Freedom

Let us turn now to a consideration of the vibrational degrees of freedom of a diatomic molecule, limiting ourselves for the present to treating small oscillations, so that the potential energy can be assumed to be a quadratic function of the deviation from equilibrium and the oscillations to be harmonic.

It is well known that the energy of a one-dimensional oscillator is determined in quantum mechanics by the formula

$$\varepsilon_n = h\nu \left(n + \frac{1}{2}\right),$$

where $\nu = \frac{1}{2\pi}\sqrt{\frac{\varkappa}{m}}$ = frequency of a relevant classical oscillator (m is the reduced atomic mass, $\varkappa$ is the quasi-elastic constant);

n = quantum number, assuming the values $n = 0, 1, 2, \ldots$.

The energy levels of the oscillator are nondegenerate, so that all $g_n = 1$.

The partition function has the form of a geometric progression

$$Z_v = \sum_{n=0}^{\infty} e^{-h\nu(n+1/2)/T},$$

and summation of the latter yields

$$Z_v = \frac{e^{-h\nu/2T}}{1 - e^{-h\nu/T}}.$$

Introducing the *characteristic vibrational temperature*

$$T_v = h\nu, \tag{48.1}$$

let us rewrite the above expression for Z_v to read

$$Z_v = \frac{e^{-T_v/2T}}{1 - e^{-T_v/T}} = \frac{e^{T_v/2T}}{e^{T_v/T} - 1}. \tag{48.2}$$

Let us consider two limiting cases.

High temperatures $T \ll T_v$. Energy quantization is immaterial in this case and the partition function must pass approximately into

the classical integral of states divided by a_v, which is the phase volume of a cell for rotational motion.

Vibrational energy is written in classical mechanics as

$$\varepsilon_v = \frac{p^2}{2m} + \frac{\varkappa q^2}{2},$$

where p = vibrational momentum ($p = m\dot{q}$);
$\varkappa$ = quasi-elastic constant;
q = generalized coordinate—the difference between the instantaneous interatomic distance r and its equilibrium value a.

The integral of states, therefore, acquires the form

$$Z_{cl} = \int_{-\infty}^{\infty} dq\, e^{-\varkappa q^2/2T} \int_{-\infty}^{\infty} dp\, e^{-p^2/2mT}.$$

Evaluating the integral, we obtain

$$Z_{cl} = 2\pi T \sqrt{\frac{m}{\varkappa}} = \frac{T}{\nu}. \tag{48.3}$$

On the other hand, at $T \gg T_v$, retaining only the first terms in the expansion of the exponential function in formula (48.2), we obtain for the partition function the expression

$$Z_v = \frac{T}{T_v}\left(1 - \frac{T_v^2}{24T^2}\right) \approx \frac{T}{T_v} = \frac{T}{h\nu}. \tag{48.4}$$

Equating this limiting value of Z_v to the quantity Z_{cl}/a_v, we find that the phase volume of a cell

$$a_v = h. \tag{48.5}$$

Thus, using the vibrational degrees of freedom as an example, we have shown once more how to determine the phase volume of a cell, $a = h^f$, where f is the number of degrees of freedom.

The energy and heat capacity of vibrational degrees of freedom are expressed in the limiting case by the formulae

$$U_v = NT^2 \frac{\partial}{\partial T}\left\{\ln\left[\frac{T}{T_v}\left(1 - \frac{T_v^2}{24T^2}\right)\right]\right\}$$

$$= NT\left(1 + \frac{1}{12}\frac{T_v^2}{T^2}\right) \approx NT, \tag{48.6}$$

$$C_v = N\left(1 - \frac{1}{12}\frac{T_v^2}{T^2}\right) \approx N \tag{48.7}$$

(C_v is the vibrational heat capacity at constant volume); the result obtained agrees with the equipartition theorem.

Low temperatures $T \ll T_v$. In this case we obtain from formula (48.2)

$$Z_v = e^{-T_v/2T}(1 + e^{-T_v/T}),$$

whence

$$U_v = NT^2 \frac{\partial}{\partial T}\left[-\frac{T_v}{2T} + \ln(1 + e^{-T_v/T})\right] = NT_v\left(\frac{1}{2} + e^{-T_v/T}\right), \quad (48.8)$$

$$C_v = N\left(\frac{T_v}{T}\right)^2 e^{-T_v/T}. \quad (48.9)$$

In accordance with Nernst theorem, $C_v \to 0$ as $T \to 0$. The internal energy of vibrational degrees of freedom tends to $NT_v/2 = Nh\nu/2$ as $T \to 0$. The latter expression represents the sum of the zero-point energies of N oscillators.

It should be noted that inasmuch as the characteristic frequencies of molecular oscillations are of the order of 10^{14} to 10^{15} s^{-1}, the characteristic vibrational temperatures of different gases lie between 10^3 and 10^4 K, i.e. the oscillations are practically frozen at room temperature and make only a small contribution to the heat capacity. Therefore for temperatures $T_r < T < T_v$ the heat capacity of gases can be calculated approximately by the formula

$$C_v = \frac{i}{2} N_A, \quad (48.10)$$

where i is the total number of translational and rotational degrees of freedom ($i = 3$ for monoatomic gases, $i = 5$ for polyatomic linear and $i = 6$ for nonlinear molecules).

It should be noted that in the temperature interval indicated the heat capacity C_V can be assumed as an approximation to be constant and the gas to be perfect. This approximation is used in phenomenological thermodynamics (Ch. I).

Let us find the non-degeneracy condition for a diatomic ideal gas and compare it to the conditions neglecting the discreteness of the energy levels of the rotational and vibrational degrees of freedom. As to the discreteness of the energy levels of translational degrees of freedom, it need not be taken into account at low temperatures, as was shown in Sec. 45. The conditions under which energy quantization need not be accounted for have the form

$$T \gg T_r = \frac{h^2}{8\pi^2 J} \quad (48.11)$$

for rotational motion and

$$T \gg T_v = h\nu \quad (48.12)$$

for vibrational motion.

Let us compare these conditions with the gas non-degeneracy requirement, i.e. with the condition for the validity of the Maxwell-Boltzmann distribution (see Sec. 37). For a polyatomic gas, just as for a monoatomic gas, this condition, according to formula (37.7), is $e^{-\mu T/} \gg 1$, and if the condition is satisfied, $e^{-\mu T}$ can be found by the formula

$$e^{-\mu/T} = \frac{g}{Na} \int e^{-\varepsilon/T} d\Gamma = \frac{g}{Na} Z_t Z_r Z_v.$$

Substituting the values of Z_t, Z_r, Z_v from formulae (40.4), (46.11) and (48.4) into the equation describing the extreme case of the Maxwell-Boltzmann distribution, we obtain the gas non-degeneracy requirement in the form

$$\frac{g}{Na} Z_t Z_r Z_v \gg 1,$$

or

$$\frac{V}{N} \left(\frac{2\pi mT}{h^2}\right)^{3/2} \frac{8\pi^2 JT}{h^2} \frac{T}{h\nu} \gg 1. \tag{48.13}$$

Substituting the numerical values of molecular gas density at atmospheric pressure, $N/V \sim 10^{19}$ cm^{-3}, of molecular mass $m \sim (10^{-23}$ to $10^{-24})$ g, of its linear dimensions $l \sim (10^{-7}$ to $10^{-8})$ cm ($J \propto ml^2$), of molecular oscillation frequencies $\nu \sim (10^{14}$ to $10^{15})$ s^{-1} and the numerical values of the constants, we obtain the estimate

$$T \gg T_{deg} \approx (10^{-16} \text{ to } 10^{-15}) \text{ erg} \sim (1 \text{ to } 10)\, K. \tag{48.14}$$

With rising pressure the gas degeneracy temperature increases in proportion to $(N/V)^{2/7} \propto P^{2/7}$, i.e. rather slowly, and this estimate could change significantly only at densities so high that the gas can no more be considered an ideal one.

Condition (48.11) at which quantization of rotational energy can be ignored is, generally speaking, stronger than the condition for the validity of the Maxwell-Boltzmann distribution, and almost coincides with it. The characteristic rotational temperatures of molecular hydrogen and deuterium, for instance, are high: 85.4 K and 43 K respectively, and in the temperature interval from ~10 K to T_r the rotational energy should be assumed to be quantized (the rotational degrees of freedom "freeze out"), and the gas to be non-degenerate. For molecular nitrogen and oxygen ($T_r = 2.85$ K and $T_r = 2.07$ K respectively) the criteria (48.11) and (48.13) practically coincide, and above the relevant temperature the gas should be assumed to be non-degenerate and the rotational energy non-quantized, with the reverse being true at lower temperatures.

Finally, condition (48.12), at which quantization of the rotational energy can be ignored, is much stronger than the non-degeneracy requirement and, as is known, it is not fulfilled for either gas. For

this reason in the temperature interval (1 to 10) K and almost up to the dissociation temperature the vibrational energy of a diatomic molecule must be assumed to be quantized (the vibrational degrees of freedom to be frozen), with the gas being described by the Boltzmann distribution.

In concluding this section let us consider the problem of the interrelation between the vibrational and rotational degrees of freedom and the changes in the thermodynamic properties of a gas caused by this interrelation.

The effect of atomic oscillation in a diatomic molecule on rotational motion manifests itself in the moment of inertia $J = mr^2$ (where m is the reduced mass and r is interatomic distance) not being constant and changing with r. The relative change in the moment of inertia is small at low temperatures, and the interrelation between oscillations and rotation can be ignored, as was done in Secs. 46, 47.

Let us estimate qualitatively the temperature T_d below which such separate treatment of oscillations and rotation is valid.

The validity condition for such individual treatment is, evidently, the fulfilment of the inequality $\overline{x^2}/l^2 \ll 1$, where $x = r - l$, and l is the mean interatomic distance. In accordance with the Maxwell-Boltzmann distribution, the probability of the interatomic distance being equal to x is proportional to $e^{-m\omega^2x^2/2T}$ and the probability is not small only when $x^2 < \frac{2T}{m\omega^2}$. Consequently, the order of magnitude of $\overline{x^2}$ is the same as that of $\frac{T}{m\omega^2}$. It follows from this that the condition for a weak interrelation between oscillations and rotation acquires the form $T \ll T_d$, $T_d \propto J\omega^2$. Substituting the values of $m \sim 10^{-24}$ g, $\omega \sim (10^{14}$ to $10^{15})$ s^{-1}, $l \sim (10^{-7}$ to $10^{-8})$ cm, we find for T_d the estimate $T_d \sim (10^{-12}$ to $10^{-8})$ erg $\sim (10^4$ to $10^8)$ K.

Thus, when dealing with small molecules built of light atoms the interrelation between oscillations and rotation must be taken into account even at temperatures of several thousand kelvins. At these temperatures, however, the atomic oscillation amplitude is of a considerable magnitude, and the oscillations can no longer be considered harmonic. The effect of the interrelation between oscillations and rotation must be treated together with the anharmonicity of oscillations. The two effects are generally of the same order.

49. Thermal Ionization of Atoms

We return in this section to the mass action law (see Sec. 31) and consider the thermal ionization of atoms. We shall limit ourselves to not very high temperatures, at which single ionization prevails. The equation of the reaction is

$$A^+ + e^- - A^0 = 0, \tag{49.1}$$

the stoichiometric coefficients being equal to $\nu_+ = 1$, $\nu_- = 1$, $\nu_A = -1$, so that the mass action law acquires the following form:

$$\frac{x_+ x_-}{x_A} = K(P, T) = P^{-\sum_i \nu_i} e^{-\sum_i \varkappa_i \nu_i / T} \tag{49.2}$$

(we have modified somewhat formula (31.8), allowing for the fact that the chemical potentials of gases are related now not to one mole, but to a single atom, and that temperature is measured in energy units).

Let us first consider the right-hand side of Eq. (49.2) and find the chemical constants for the gases of neutral atoms, ions and electrons, assuming the three gases to be monoatomic, so that only translational degrees of freedom exist. Hence, the chemical potentials of the three gases can be found by formula (40.5). An additional term will, however, be added to the expressions for the chemical potentials of atoms and ions, ε_{0i}, representing the ground energy of the electron shell of the ith atom (ion). While a "pure" gas was being considered, the ground energy could be selected so as to serve as a reference point. But this becomes impossible for a mixture of gases, since the quantity ε_{0i} is not the same for different gases.

Thus, μ_i is expressed by the formula

$$\mu_i = T \ln \left[\frac{N_i}{g_i V} \left(\frac{h^2}{2\pi m_i} \right)^{3/2} \right] + \varepsilon_{0i}$$

$$= T \ln P_i + \varepsilon_{0i} - \frac{5}{2} T \ln T + T \ln \left[\frac{1}{g_i} \left(\frac{h^2}{2\pi m_i} \right)^{3/2} \right], \tag{49.3}$$

whence the chemical constants in formula (31.5) are

$$\chi_i = \varepsilon_{0i} - \frac{5}{2} T \ln T + T \ln \left[\frac{1}{g_i} \left(\frac{h^2}{2\pi m_i} \right)^{3/2} \right]. \tag{49.4}$$

The term $\sum_i \nu_i \chi_i$ in the exponent in formula (49.2) is found to be expressed by

$$\sum_i \nu_i \chi_i = I - \frac{5}{2} T \ln T + \frac{3}{2} T \ln \frac{h^2}{2\pi m} - T \ln \frac{2g_+}{g_A},$$

where $I = \varepsilon_{0A^+} - \varepsilon_{0A}$ is the ionization energy; m is the mass of the electron (the terms containing m_A and m_{A^+} vanish, since $m_{A^+} \approx m_A$) and the factors 2, g_+ and g_A in the last term are the degeneracies for an electron and the ground electronic levels of an ion and an atom.

Allowing for $\sum_i \nu_i = 1$ and making use of the equation of state $P = NT/V$, we obtain for the reaction constant the expression

$$K(P, T) = \frac{1}{P} \frac{2g_+}{g_A} \left(\frac{2\pi m}{h^2} \right)^{3/2} T^{5/2} e^{-I/T} = \frac{V}{N} \frac{2g_+}{g_A} \left(\frac{2\pi m}{h^2} \right)^{3/2} T^{3/2} e^{-I/T}.$$

Let us consider now the left-hand side of (49.2) and express all the concentrations in terms of the number of ions N_+ (which is equal to the number of electrons N_-) and the total number of heavy particles, both ionized and neutral, N_0, which is plainly constant. We have

$$x_+ = x_- = \frac{N_+}{N}, \qquad x_A = \frac{N_A}{N},$$

where the total number of particles N and the number of neutral atoms N_A are expressed in terms of chosen variables:

$$N_A = N_0 - N_+, \quad N = 2N_+ + N_A = N_0 + N_+.$$

Consequently, the concentrations x_+, x_-, x_A are equal to

$$x_+ = x_- = \frac{N_+}{N_0 + N_+}, \quad x_A = \frac{N_0 - N_+}{N_0 + N_+}. \tag{49.5}$$

Introducing the degree of ionization $\alpha = \frac{N_+}{N_0}$, the mass action law can be rewritten to read

$$\frac{\alpha^2}{1-\alpha} = 2\varphi(T, V), \tag{49.6}$$

where $\varphi(T, V)$ is a dimensionless function

$$\varphi(T, V) = \frac{g_+}{g_A} \frac{V}{N_0} \left(\frac{2\pi mT}{h^2}\right)^{3/2} e^{-I/T}. \tag{49.7}$$

It should be noted that if in formula (49.4) pressure is not expressed in terms of temperature and volume, the degree of ionization is described by another equation

$$\frac{\alpha^2}{1-\alpha^2} = P^{-1}K(T),$$

from which follows *Saha's equation*

$$\alpha = \frac{1}{\sqrt{1 + P^{-1}K(T)}}, \tag{49.8}$$

defining the degree of ionization as a function of pressure and temperature. Equation (49.6) is more convenient if the ionized gas is confined within a vessel of fixed volume. The solution of this equation has the following form:

$$\alpha(T, V) = -\varphi(T, V) + \sqrt{\varphi^2(T, V) + 2\varphi(T, V)}. \tag{49.9}$$

It follows from Eq. (49.9) that there is a critical temperature T_{cr} in the neighbourhood of which the function $\varphi(T, V)$ is close to unity. At $T \gg T_{cr}$ we have $\varphi(T, V) \gg 1$ and, expanding the term $(1 + 2\varphi^{-1})^{1/2}$, we find from Eq. (49.9) the degree of ionization to be

close to unity, $\alpha(T, V) = 1 - \frac{1}{2}\varphi^{-1}$. At $T \ll T_{cr}$, $\varphi(T, V) \ll 1$ and $\alpha(T, V) = \sqrt{2\varphi(T, V)} \ll 1$, indicating that the degree of ionization is small. Let us estimate the magnitude of the critical temperature T_{cr}, rewriting for this purpose Eq. (49.7) in the form

$$\varphi(T, V) = \left(\frac{T}{T_0}\right)^{3/2} e^{-I/T},$$

were the temperature denoted by T_0 equals

$$T_0 = \left(\frac{g_A}{g_+}\right)^{2/3} \left(\frac{N_0}{V}\right)^{2/3} \frac{h^2}{2\pi m}.$$

It should be noted that temperature T_0 is usually very small, no more than a few degrees on the absolute temperature scale for plasma with a density of 10^{15} cm^{-3}. In contrast, the temperature corresponding to the ionization energy I is quite high, being of the order of tens of electronvolts or (10^5 to 10^6) K. Equating the function $\varphi(T, V)$ to unity, we obtain the equation

$$\frac{I}{T_{cr}} = \frac{3}{2} \ln \frac{T_{cr}}{T_0}, \quad \text{or} \quad \frac{I}{T_{cr}} = \frac{3}{2} \ln \frac{I}{T_0} - \frac{3}{2} \ln \frac{I}{T_{cr}}.$$

With the account taken of the large magnitude of the parameter I/T_{cr}, the approximate solution of the above equation is

$$T_{cr} = \frac{I}{\frac{3}{2} \ln (I/T_0)}.$$

The temperature at which a considerable proportion of atoms is ionized is much lower than the ionization energy I, by $\frac{3}{2} \ln (I/T_0)$ times.

The physical reason for this can be easily understood when it is considered that the two-level effect must manifest itself in this problem as well: in addition to the energy of translational motion continuously varying with temperature and the effect due to the change in the number of particles because of ionization, there are two levels of internal energy of the atom and the ion, differing from one another by I. This effect manifests itself most vividly as a result of the fact that the ratio γ of the statistical weights of the final state of the electron lying in the continuous spectrum and of the initial state of the electron in an atom, associated with the discrete spectrum, is rather small. The estimate of this ratio is

$$\gamma \approx \frac{2g_+}{g_A} \frac{\frac{4}{3}\pi \bar{p}^3 V}{h^3},$$

where $\bar{p}$ is the mean momentum of the free electron. Substituting $\bar{p} \approx (2mT)^{1/2}$, we find

$$\gamma \approx \frac{2g_+}{g_A} V \left(\frac{mT}{h^2}\right)^{3/2}.$$

which coincides with the pre-exponential factors in Eq. (49.7), accurate to the numerical coefficients.

In this way the two-level effect explains the high value of the pre-exponential factor (the smallness of the parameter T_0), responsible for the "shift" of the beginning of ionization in the direction of temperatures lower than I.

The reader can confirm for himself that the heat capacity of an ionized gas, C_V, plainly tending to a value of $\frac{3}{2}N_A$ at low temperatures (non-ionized gas) and to a value $3N_A$ at high temperatures (completely ionized gas), has a sharp maximum at $T \sim T_{cr}$—the two-level effect.

Problems

1. Find the "rate" of single ionization, $\frac{d\alpha}{dT}$, estimate the temperature at which ionization is maximum and the temperature interval in which $\frac{d\alpha}{dT}$ markedly differs from zero. Plot the graph of the dependence $\alpha = \alpha(T)$.

Answer. $\alpha' = \left(\frac{3}{2} + \frac{I}{T}\right) \frac{\varphi}{T} \frac{\varphi + 1 - \sqrt{\varphi^2 + 2\varphi}}{\sqrt{\varphi^2 + 2\varphi}}$ (Fig. 66),

$$\alpha' = \begin{cases} \frac{3/2 + I/T}{2\varphi T} \ll \frac{1}{T} & \text{at } T \gg T_{cr}, \\ \frac{I}{\sqrt{2}\, T^2} \sqrt{\varphi} \ll \frac{1}{T} & \text{at } T \ll T_{cr}, \end{cases}$$

$$\Delta T = \frac{1}{\alpha'(T_{cr})} \approx \frac{6T_{cr}^2}{I} = \frac{8I}{3 \ln^2 (I/T_0)}.$$

2. Find the heat capacity of singly-ionized plasma and investigate the dependence of its behaviour on temperature. Consider the limiting cases $T \ll T_{cr}$ and $T \gg T_{cr}$. Assuming $I/T_{max} \gg 1$, estimate approximately the temperature T_{max} at which the heat capacity is maximum, and also $C_{V\,max}$.

Answer. $\frac{C_V}{N_0} = \frac{3}{2}\left(1 - \varphi + \sqrt{\varphi^2 + 2\varphi}\right)$

$$+ \left(\frac{3}{2} + \frac{I}{T}\right)^2 \varphi \frac{\varphi + 1 - \sqrt{\varphi^2 + 2\varphi}}{\sqrt{\varphi^2 + 2\varphi}} \quad \text{(Fig. 67)},$$

$$\frac{C_V}{N_0} = \begin{cases} \frac{3}{2}\left[1+\left(\frac{I}{T}\right)^2\left(\frac{2\varphi}{9}\right)^{1/2}\right] & \text{at } T \ll T_{cr}, \\ 3\left[1+\frac{1}{6}\left(\frac{I}{T}\right)^2\frac{1}{\varphi}\right] & \text{at } T \gg T_{cr}, \end{cases}$$

$$T_{max} \sim T_{cr}, \quad \frac{C_{V\,max}}{N_0} \sim \left(\frac{I}{T_{max}}\right)^2 \varphi_{max}^2 \gg 1.$$

Hint. The temperature corresponding to maximum heat capacity is found from the equation $\varphi_{max} = \sqrt{2} - 1 \approx 0.41$. To find $C_{V\,max}$, leave only the term $\sim (I/T)^2$ in the expression for C_V/N_0 and find its maximum value.

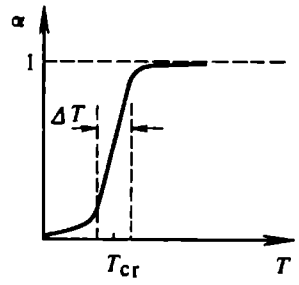


FIG. 66

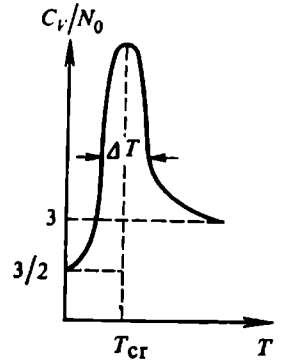


FIG. 67

50. Thermal Dissociation of Molecules

Making use of the mass action law, let us consider in this section the problem of the dissociation of a molecule consisting of two like atoms:

$$2A - A_2 = 0. \tag{50.1}$$

The stoichiometric coefficients $\nu_A = 2$, $\nu_{A_2} = -1$ and for this reaction the mass action law has the form

$$\frac{x_A^2}{x_{A_2}} = P^{-\sum_i \nu_i} e^{-\sum_i \nu_i \chi_i/T} = P^{-1} e^{(\chi_{A_2} - 2\chi_A)/T}. \tag{50.2}$$

The essential feature of the problem being considered is that, strictly speaking, it cannot be solved with the aid of vibrational thermodynamic functions calculated in a harmonic approximation. Indeed, if in the expansion of potential energy we limit ourselves to the terms that are quadratic in the deviation from equilibrium inter-

atomic distance, then in such an (oscillator) potential field (curve *1* in Fig. 68) only finite motion of atoms is possible with a discrete energy spectrum, and the dissociation of a molecule into atoms cannot be described in this approximation. Strictly speaking, dissociation can be described by accounting for the anharmonicity of oscillation and also for the link between oscillations and rotations. Then, a potential barrier appears (curve *2* in Fig. 68) and the transtion to a continuous spectrum becomes possible—the relative motion of atoms becomes infinite. Such a rigorous solution of the problem of dissociation is, however, rather intricate and cumbrous (see, for instance, [9]) and we shall limit ourselves to a less strict, but simpler method of solving the problem.

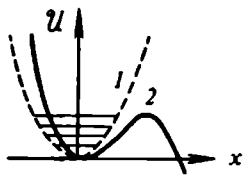


FIG. 68

We shall consider vibrational thermodynamic functions in a harmonic approximation, assuming that not all oscillator levels become excited, but only p lower levels ($p \sim 5$ to 10), with higher-lying "levels" being already arranged in the continuous spectrum region. In this approximation we have

$$Z_V = \sum_{n=0}^{p} e^{-(n+1/2)\,T_V/T} = \frac{e^{-T_V/2T}\left(1-e^{-(p+1)\,T_V/T}\right)}{1-e^{-T_V/T}} \tag{50.3}$$

and

$$\mu_V = -T \ln Z_V = \frac{T_V}{2} + T \ln \frac{1-e^{-T_V/T}}{1-e^{-(p+1)\,T_V/T}}\,. \tag{50.4}$$

For χ_{A_2} we obtain

$$\ln \chi_{A_2} = \varepsilon_{0i} + \frac{h\nu}{2} - \frac{7}{2} T \ln T + T \ln \frac{1-e^{-h\nu/T}}{1-e^{-(p+1)\,h\nu/T}} + T \ln \left[\left(\frac{h^2}{4\pi m} \right)^{3/2} \frac{h^2}{2\pi^2 m l^2 g_{A_2}} \right]. \tag{50.5}$$

Making use of expression (49.4) for χ_A and of the equation of state $P = NT/V$, we find for the right-hand side of Eq. (50.2) the expression

$$\frac{g_A^2}{2g_{A_2}hl^2} \left(\frac{m}{\pi} \right)^{1/2} \frac{V}{N}\, T^{1/2}\, \frac{1-e^{-\nu h/T}}{1-e^{-(p+1)\,h\nu/T}}\, e^{-I/T}, \tag{50.6}$$

where $I = 2\varepsilon_{0A} - \varepsilon_{0A_2} - h\nu/2$ = dissociation energy;
l = mean molecular size.

Introducing as a variable the degree of dissociation $\alpha = N_A/N_0$, where $N_0 = N_A + 2N_{A_2}$ is the constant total number of atoms, we obtain for the total number of particles the expression

$$N = N_A + N_{A_2} = N_0 \frac{1+\alpha}{2}$$

and for the concentrations x_A and x_{A_2} the expressions

$$x_A = \frac{2\alpha}{1+\alpha}, \quad x_{A_2} = \frac{1-\alpha}{1+\alpha}.$$

Equation (50.2) acquires a form similar to that of Eq. (49.6):

$$\frac{\alpha^2}{1-\alpha} = 2\varphi(T, V), \tag{50.7}$$

where

$$\varphi(T, V) = \frac{g_A^2 (m/\pi)^{1/2} V}{16 g_{A_2} \hbar l^2 N_0} T^{1/2} \frac{1-e^{-h\nu/T}}{1-e^{-(1+p)h\nu/T}} e^{-I/T}. \tag{50.8}$$

Further reasonings are similar to those described in detail in the preceding section, and so only the results will be set out here, leaving to the reader the relevant calculations by means of solving the problems for this section.

The method of solving Eq. (50.7) depends on whether the value of the function $\varphi(T, V)$ is large or small. Denote by T_{cr} the temperature at which $\varphi(T_{cr}, V) \approx 1$. Then, at $T \ll T_{cr}$

$$\varphi(T, V) \approx \frac{g_A^2}{16 g_{A_2} \hbar l^2} \left(\frac{m}{\pi}\right)^{1/2} \frac{V}{N_0} T^{1/2} e^{-I/T} \ll 1.$$

The temperature $h\nu$ is of the same order of magnitude as the dissociation energy equalling about (10^5 to 10^6) K with $\alpha \approx \sqrt{2\varphi} \ll 1$. At $T > T_{cr}$ the function $\varphi(T, V)$ increases (although rather slowly) and assumes the value $\varphi > 1$. The degree of dissociation then acquires the order of $\alpha \sim 1 - 1/2\ \varphi^{-1}$. The critical temperature T_{cr} is specified by the equation

$$\left(\frac{T_{cr}}{T_0}\right)^{1/2} \frac{1-e^{-h\nu/T}}{1-e^{-(p+1)h\nu/T}} e^{-I/T_{cr}} \sim 1, \tag{50.9}$$

where $T_0 = \left(\frac{16 g_{A_2}}{g_A^2} \frac{\hbar l^2 N_0}{V}\right)^2 \frac{I}{m}$. The approximate solution of this equation has the form

$$T_{cr} \approx \frac{I}{\frac{1}{2} \ln (I/T_0)} \tag{50.10}$$

(the terms $e^{-h\nu/T}$ and $e^{-(p+1)h\nu/T}$ are rather small at $T \sim T_{cr}$), and, as in the preceding section, we arrive at the conclusion that

dissociation proceeds actively at temperatures that are several times lower than I. This is again traced to the two-level effect and to the large statistical weight of the states with continuous-spectrum compared to the statistical weight of the bound state.

Problems

1. Prove formula (50.10).
2. Find the derivative $\frac{d\alpha}{dT}$ and estimate the width ΔT of the interval within which dissociation proceeds at a noticeable rate.

Answer. $\frac{d\alpha}{dT}=\left(\frac{1}{2}+\frac{I}{T}\right)\frac{\varphi}{T}\frac{\varphi+1-\sqrt{\varphi^2+2\varphi}}{\sqrt{\varphi^2+2\varphi}}$

$$\frac{d\alpha}{dT}=\begin{cases}\dfrac{I\sqrt{\varphi}}{\sqrt{2}T^2}\ll\dfrac{1}{T} & \text{at } T\ll T_{cr},\\ \left(\dfrac{1}{2}+\dfrac{I}{T}\right)\dfrac{1}{2T\varphi}\ll\dfrac{1}{T} & \text{at } T\gg T_{cr},\end{cases}$$

$$\Delta T\sim\left(\frac{d\alpha}{dT}\right)_{cr}^{-1}\approx\frac{6T_{cr}^2}{I}=\frac{24I}{\ln^2(I/T_0)}$$

3. Find the heat capacity of a partly dissociated gas and investigate its dependence on temperature.

Answer. $\frac{C_V}{N_0}=\frac{1}{2}\left[\frac{5}{2}+\frac{1}{2}\alpha+\left(\frac{T}{2}+I\right)\frac{d\alpha}{dT}\right]$

$$C_V\approx\begin{cases}\dfrac{5}{4}N_0 & \text{at } T\ll T_{cr},\\ \dfrac{3}{2}N_0 & \text{at } T\gg T_{cr},\\ \dfrac{N_0}{48}\ln^2\dfrac{I}{T_{cr}}\gg\dfrac{3}{2}N_0 & \text{at } T\sim T_{cr}.\end{cases}$$

51. Paramagnetic Gas in a Magnetic Field

Let us consider a gas consisting of molecules having a constant magnetic moment μ and placed in a homogeneous permanent magnetic field of intensity H.

The potential energy of such a molecule is determined by the formula

$$\mathcal{U}(\theta)=-\mu H, \tag{51.1}$$

where θ is the angle between the directions of μ and H. Inasmuch as the potential energy depends only on the direction of the magnetic moment μ, the molecules are uniformly distributed in space.

Consider first classical particles for which the spatial direction of the magnetic moments may continuously vary so that any orientation of the moment is possible. The distribution of molecules over the directions of μ is given by the Boltzmann formula (42.1)

$$\frac{dN}{N} = \frac{e^{-\beta \mathcal{U}(\theta)} d\Omega}{\int e^{-\beta \mathcal{U}(\theta)} d\Omega},$$

where $d\Omega = \sin\theta\, d\theta\, d\varphi$ is an elementary solid angle. Integrating this expression over φ, we obtain the distribution in θ:

$$\frac{dN(\theta)}{N} = \frac{\exp[\beta\mu H\cos\theta]\sin\theta\, d\theta}{\int_0^\pi \exp[\beta\mu H\cos\theta]\sin\theta\, d\theta}. \tag{51.2}$$

The integral in the denominator is equal to

$$Z(\beta) = \int_0^\pi \exp[\beta\mu H\cos\theta]\sin\theta\, d\theta = \frac{2\sinh(\beta\mu H)}{\beta\mu H}. \tag{51.3}$$

Let us find the average value of the projection of the magnetic moment on the direction of the field. It is clear that the mean values of the projection of the magnetic moment in directions perpendicular to the field are equal to zero. In this case

$$\overline{\mu\cos\theta} = \mu\int \cos\theta \frac{dN(\theta)}{N} = \mu \frac{\int_0^\pi \exp[\beta\mu H\cos\theta]\cos\theta\sin\theta\, d\theta}{\int_0^\pi \exp[\beta\mu H\cos\theta]\sin\theta\, d\theta} = \frac{1}{H}\frac{\partial}{\partial\beta}\ln Z(\beta).$$

Substituting the value of Z from (51.3), we find that

$$\overline{\mu\cos\theta} = \frac{1}{H}\frac{\partial}{\partial\beta}\ln\frac{\sinh(\beta\mu H)}{\beta} = \mu\left[\coth(\beta\mu H) - \frac{1}{\beta\mu H}\right].$$

Introducing the notation $L(x) = \coth x - 1/x$, we find that the magnetization $M = N\overline{\mu\cos\theta}$ is equal to

$$M = N\mu L\left(\frac{\mu H}{T}\right) = M_0 L\left(\frac{\mu H}{T}\right), \tag{51.4}$$

where $M_0 = N\mu$ is the maximum magnetization reached as $H \to \infty$ or $T \to 0$. The function $L(x)$, referred to as the *Langevin function*, characterizes the degree of orientation of elementary magnetic moments for a given field and temperature. The implicit form of this function has already been used in Sec. 15. The parameter $x =$

$= \frac{\mu H}{T} = \frac{M_0 H}{N_A T}$ represents by the order of magnitude the ratio of the mean magnetic energy to the mean energy of thermal motion.

Let us consider in greater detail the behaviour of the function $L(x)$ in two limiting cases.

Strong fields and low temperatures, $x = \mu H/T \gg 1$. **In this case**

$$L(x) \approx 1 - \frac{1}{x} \xrightarrow[x \to \infty]{} 1, \tag{51.5}$$

and the *saturation* takes place, i.e. magnetization is maximum in the case of strong field and low temperatures.

Weak fields and high temperatures, $x = \mu H/T \ll 1$. **In this case, expanding** the exponentials $e^{\pm x}$ in powers of x **up to terms** $\sim x^3$, **we obtain**

$$\coth x \approx \frac{1}{x}\left(1 + \frac{x^2}{3}\right), \quad L(x) \approx \frac{x}{3} \ll 1. \tag{51.6}$$

The degree of the magnetic dipole orientation is small with weak fields and high temperatures. It can be seen that the parameter $L'(0)$, used in Sec. 15, is equal to $L'(0) = \frac{1}{3}$.

Formula (51.4) is purely classical and does not account for the quantization of magnetic-moment projections. The projection of the magnetic moment of an electron in the direction of a magnetic field is shown in quantum mechanics to assume only discrete values. For an unbound particle with spin j, for instance, the projection can be equal to $-\mu, -\mu\frac{j-1}{j}, \ldots, \mu\frac{j-1}{j}, \mu$, where μ is the maximum value of the magnetic moment projection, equal to

$$\mu = \frac{eh}{2\pi mc} j = 2\mu_B j, \tag{51.7}$$

where $\mu_B = \frac{eh}{4\pi mc}$ = Bohr magneton;

j = spin quantum number, which can be both an integer and half-integer.

The expression for $\bar{\mu}_z = \overline{\mu \cos\theta}$ is

$$\bar{\mu}_z = \frac{\mu \sum\limits_{s=-j}^{j} \frac{s}{j} e^{\beta\mu H s/j}}{\sum\limits_{s=-j}^{j} e^{\beta\mu H s/j}} = \frac{1}{H}\frac{\partial}{\partial\beta}\left(\ln \sum_{s=-j}^{j} e^{\beta\mu H s/j}\right).$$

The sum of the geometric progression under the logarithm sign is equal to

$$\frac{\sinh\left[\beta\mu H\left(1+\frac{1}{2j}\right)\right]}{\sinh\left(\beta\mu H/2j\right)},$$

and magnetization is expressed by

$$M = M_0 L_j(\beta\mu H) = M_0 L_j(\mu H/T), \tag{51.8}$$

where the *Langevin quantum functions* $L_j(\mu H/T)$, also referred to as Brillouin functions, are determined by the formula

$$L_j(x) = \left(1+\frac{1}{2j}\right)\coth\left[\left(1+\frac{1}{2j}\right)x\right] - \frac{1}{2j}\coth\left(\frac{x}{2j}\right) \tag{51.9}$$

and depend essentially on j. It should be noted, however, that all quantum functions $L_j(x) \xrightarrow[x\to\infty]{} 1$ (strong fields and low temperatures), which leads to the saturation effect—maximum magnetization. In fact, as $x \to \infty$, $\coth ax \to 1$ and, according to (51.9), $L_j(x) \to 1$. In the reverse limiting case $x \ll 1$ (weak fields and high temperatures) expansion (51.6) gives

$$L_j(x) = \frac{j+1}{3j}x \ll 1, \tag{51.10}$$

and the magnetization is weak.

The slope of the curve $L_j(x)$ is equal to $L'(0) = \frac{j+1}{3j}$ at the coordinate origin and depends essentially on j. In particular, at $j = \frac{1}{2}$ (electron gas, for instance) we have

$$M = M_0 L_{1/2}\left(\frac{\mu H}{T}\right) = M_0 \tanh\left(\frac{\mu H}{T}\right), \quad L'_{1/2}(0) = 1. \tag{51.11}$$

It can readily be seen that the classical Langevin function $L(x)$ is the limit of the function $L_j(x)$ as $j \to \infty$.

CHAPTER V

DEGENERATE GASES

52. Equilibrium Thermal Radiation. Photon Gas

Let us first consider within the framework of classical ideas equilibrium radiation in a cavity whose walls are at a temperature T. From the viewpoint of classical physics equilibrium radiation in a cavity is a system of standing waves with different frequencies ν, and different propagation and polarization directions. The object here is to solve the problem that could not be solved by the methods of phenomenological thermodynamics (see Sec. 17), i.e. to find the spectral radiant energy density $\rho(\nu, T)$.

We shall base our reasonings on the energy equipartition law (see Sec. 43), according to which each vibrational degree of freedom (each elementary wave) makes a contribution to the mean energy, equal to T. For this reason, in order to determine $\rho(\nu, T)$, it is necessary to find the number of different standing waves per unit volume with frequencies in the range between ν and $\nu + d\nu$, and multiply this number by T. Assume for the sake of simplicity that the cavity is a cube with edges of length l orientated along the coordinate axes (it is clear that the result cannot depend on the shape of the cavity).

The equation of a standing wave is

$$= \mathbf{A} \sin(\mathbf{fr} + \delta), \tag{52.1}$$

where y means either an electric or magnetic field of the wave and f is a wave vector the direction of which coincides with the direction of wave propagation, and its magnitude is $f = 2\pi/\lambda = 2\pi\nu/c$; δ is the initial phase and A is the wave amplitude. Let us impose periodic boundary conditions stating that a whole number of waves can fit along each of the cube edges. Physically this is associated with the fact that either nodes or loops of the standing waves are observed at the walls, depending on the reflecting properties of the walls. Whence, the conditions

$$f_i l = m_i \cdot 2\pi, \quad i = 1, 2, 3, \ldots, \quad m_i = 0, \pm 1, \pm 2, \ldots \tag{52.2}$$

(f_i are the projections of a wave vector). The wave frequencies assume, consequently, quantized values

$$\nu = \frac{cf}{2\pi} = \frac{c}{l} m = \frac{c}{l} \sqrt{m_1^2 + m_2^2 + m_3^2}. \tag{52.3}$$

Let us introduce the space of numbers m_1, m_2, m_3 (Fig. 69) and denote by $dn(\nu)$ the number of various waves with frequencies ranging between ν and $\nu + d\nu$, equal to the doubled (at the expense of two independent polarizations) number of integer coordinates m_i between the spheres

with radii m and $m + dm$. Since for each such point there is a cube of unit edge (unit volume), the required number of points equals, with great accuracy, the volume between the indicated spheres. Therefore,

$$dn(\nu) = 2 \cdot 4\pi m^2\, dm = \frac{8\pi l^3}{c^3} \nu^2\, d\nu. \tag{52.4}$$

Assuming in formula (52.4) $l^3 = V = 1$ and multiplying by T, we find the spectral radiant energy density

$$\rho(\nu, T) = \frac{8\pi T}{c^3} \nu^2. \tag{52.5}$$

Formula (52.5) expresses the Rayleigh-Jeans law. The physical corollaries of this law were discussed in Sec. 17, where formula (52.5) was seen to be unsound.

Let us consider now radiation as a gas of light quanta, or photons, possessing the following properties. Photons move with the velocity of sound in a vacuum and are, therefore, particles with zero rest mass, $m_0 = 0$ (which follows, even if only from the energy formula $E = m_0c^2/\sqrt{1 - v^2/c^2}$). The relationship between energy and momentum, which for "ordinary" particles with $m_0 \neq 0$ is expressed by $E^2 = m_0^2c^4 + p^2c^2$, is expressed by $E = cp$ in the case of photons. Photons have integer spin equal to unity, and they are, therefore, bosons, meaning that the number of photons in an elementary cell is not limited and can have any value. Furthermore, since photons are emitted continuously and absorbed again by the cavity walls, the total number of photons is not fixed, and the condition $\sum_i N_i = N$ is not applicable to a photon gas. For this reason the Lagrange factor α and the chemical potential associated with it are not involved in the problem under consideration. The formal meaning of this is that in the Bose-Einstein distribution for photons the chemical potential, related to α by the formula $\mu = \alpha T$, must be chosen equal to zero and

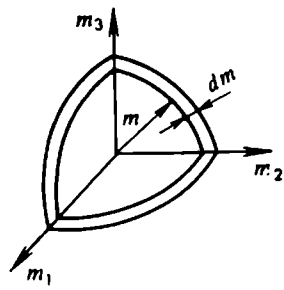


FIG. 69

$$dN = \frac{2\, d\Gamma/a}{e^{\varepsilon/T} - 1}. \tag{52.6}$$

Thus, of the two equations

$$N = \int \frac{2\,d\Gamma}{a\,(e^{\varepsilon/T}-1)}, \quad U = \int \frac{2\varepsilon\,d\Gamma}{a\,(e^{\varepsilon/T}-1)}$$

the first changes its purpose. It defines not the chemical potential for a photon gas, which is exactly equal to zero, but the average number of photons in volume V.

Substituting $d\Gamma = 4\pi p^2\,dp\,dV = 4\pi\varepsilon^2\,d\varepsilon\,dV/c^3$, integrating over the volume and assuming $V = 1$, we obtain for the radiant energy density the following expression:

$$\rho(\varepsilon, T) = \frac{8\pi}{c^3 a}\frac{\varepsilon^3}{e^{\varepsilon/T}-1}. \tag{52.7}$$

Integrating with respect to ε, we find for the volume energy density the expression

$$u(T) = \int_0^\infty \rho(\varepsilon, T)\,d\varepsilon = \frac{8\pi}{c^3 a}\int_0^\infty \frac{\varepsilon^3\,d\varepsilon}{e^{\varepsilon/T}-1} = \frac{8\pi K_3}{c^3 a}T^4, \tag{52.8}$$

where $K_3 = \pi^4/15$ [see Mathematical Appendix, formula (VII.3)]. The formula thus derived expresses the Stefan-Boltzmann law (see Sec. 17)

$$u = \sigma T^4 \tag{52.9}$$

and the expression for the constant σ is

$$\sigma = \frac{8\pi^5 k^4}{15c^3 a}, \tag{52.10}$$

where T is measured not in energy units but in kelvins, k is the Boltzmann constant.

It follows from the above that the cell volume a is expressed by

$$a = \frac{8\pi^5 k^4}{15c^3\sigma} \tag{52.11}$$

and is measured in cubed units of action; substituting $\sigma = 7.56 \times 10^{-15}$ erg/cm$^3\cdot$K found by experiment, we obtain with a very high degree of accuracy*

$$a = 279.72 \times 10^{-91}\ \text{erg}^3\text{s}^3 = h^3.$$

* Attention is drawn to the fact that the quantum constant h is not present in formula (52.11) and the cell volume a is found from the essentially classical formulae (52.6) through (52.9), which do not account for energy quantization but are based on the particle indistinguishability principle (the Bose-Einstein distribution). By contrast, in Secs. 45, 46 and 48, the volume of a cell was determined within the framework of the particle distinguishability hypothesis (the Maxwell-Boltzmann distribution), but with energy quantization being taken into account, meaning that the constant h was always present in the formulae employed.

It should be noted that if we return to the energy temperature scale and substitute the found value of $a = h^3$, the coefficient in the Stefan-Boltzmann law $u(T) = \sigma' T^4$ will be equal to $\sigma' = \frac{8\pi^5}{15h^3c^3} = \frac{\pi^2\alpha^3}{15e^6}$, where $\alpha = \frac{2\pi e^2}{hc} \approx \frac{1}{137}$ is the fine structure constant. Dirac found (unpublished report) σ' to be equal to $(4\pi e)^{-6}$, accurate to five decimal places. It follows that the reciprocal of the fine structure constant is expressed by

$$\alpha^{-1} = 137 = 4\pi^2 \left(\frac{\pi^3}{1 \cdot 3 \cdot 5}\right)^{1/3}, \qquad (52.12)$$

which is true to a very high degree of accuracy. This coincidence is interpreted by Dirac in the following way. Classical electrodynamics, like modern quantum electrodynamics, treats the concept of electrical charge quantization as a foreign concept introduced from outside, i.e. from the viewpoint of electrodynamics an electron could carry a charge as small as desired. But as $e \to 0$, we would have $\sigma' \to \infty$.

The coming theory of elementary particles must elucidate the reasons for charge quantization and establish the meaning of the expression $\frac{hc}{2\pi e^2} = 137$, relating relativism ($c$), quantization ($h$) and the theory of elementary particles (e).

At the same time, there are reasons to believe that even in this theory of elementary particles the expressions for σ' and α will cease to be simple coincidences and will be rationally explained. It is of interest to note that at one time many papers appeared, in which the authors proceeded from the fact that the quantity $\alpha^{-1} = 137$ is an integer, and endeavoured in different ways to impart a physical meaning to this quantity. If Dirac's idea is accepted, then, according to formula (52.12), α^{-1} is not an integer, but merely a number that has "disguised itself" as an integer with a high accuracy, and that the reasonings based on it being an integer have no meaning.

Let us make use now of Planck's formulae relating the photon energy and momentum with light wave frequency, $\varepsilon = h\nu$, $p = h\nu/c$. These formulae express the wave-particle duality of light, with the conversion factor h being used when passing from a wave description to a corpuscular one. The Bose-Einstein distribution (52.6) then acquires the form

$$dN(\nu) = \frac{8\pi}{c^3} \frac{\nu^2 d\nu\, dV}{e^{h\nu/T} - 1}, \qquad (52.13)$$

and for the spectral radiant energy density we obtain

$$\rho(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/T} - 1}. \qquad (52.14)$$

Formula (52.14), referred to as *Planck's formula*, played a major role in the development of physics at the beginning of the twentieth century. Planck was the first to use quantum ideas in his theory of radiation, which then developed into the harmonious, well-composed and all-embracing theory of microprocesses-quantum mechanics and quantum field theory.

Let us consider two limiting cases. In the low-frequency band, when $h\nu/T \ll 1$, by expanding the denominator in formula (52.14) we find that

$$\rho(\nu, T) = \frac{8\pi T}{c^3}\nu^2. \tag{52.15}$$

It is natural that in this limiting case of low-energy photons the corpuscular properties of light do not manifest themselves, and the derived formula coincides with the classical Rayleigh-Jeans law.

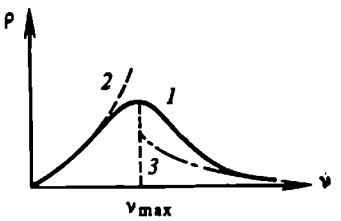


FIG. 70

In the opposite limiting case, when $h\nu/T \gg 1$, Planck's formula reduces to

$$\rho(\nu, T) = \frac{8\pi h}{c^3}\nu^3 e^{-h\nu/T}, \tag{52.16}$$

This formula was suggested by Wien and agrees well with experimental data for high frequencies.

The dependence $\rho(\nu)$ is plotted in Fig. 70 at a fixed temperature $T = \text{const}$ in accordance with Planck's formula (curve *1*). For comparison $\rho(\nu)$ according to Rayleigh-Jeans' formula is shown as a dotted line (curve *2*), while a dot-and-dash line represents the same dependence in accordance with Wien's formula (curve *3*).

Wien's displacement law is a corollary of Planck's formula (see Sec. 17). In contrast to phenomenological thermodynamics, statistical physics makes possible the determination of the numerical value of the constant b, referred to as Wien's constant.

Proceeding in a regular manner, we find the maximum of the expression (52.14). We have

$$\left(\frac{\partial \rho}{\partial \nu}\right)_T = \frac{8\pi h}{c^3}\frac{\nu^2}{e^{h\nu/T}-1}\left[3 - \frac{\frac{h\nu}{T}e^{h\nu/T}}{e^{h\nu/T}-1}\right].$$

The frequency corresponding to the maximum $\rho(\nu, T)$ is obtained by equating the expression in square brackets to zero. Introducing the variable $y = h\nu_{\max}/T$, we find the equation

$$3(e^y - 1) = ye^y,$$

which has only one root, equal approximately to $y = 2.85$. From this follows Wien's displacement law in the form $\nu_{max}/T = b$, where Wien's constant b equals $2.85/h$.

Let us now derive the formula relating radiation pressure to the volume energy density,

$$P = \frac{1}{3} u(T),$$

which was used in Sec. 17 in studying the thermodynamic properties of equilibrium radiation. Since the expression for the internal energy was found in the foreign variables T, V ($U = \sigma T^4 V$), to find the equation of state $P = P(V, T)$, as well as the entropy of radiation, it is convenient to pass to the Ω-potential. Using formula (38.16), we obtain

$$\Omega = -\frac{1}{3} U(T) = -\frac{1}{3} u(T) V, \tag{52.17}$$

whence we find

$$P = -\frac{\Omega}{V} = \frac{1}{3} u(T) = \frac{\sigma T^4}{3}, \tag{52.18}$$

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_V = \frac{1}{3} u'(T) V = \frac{4}{3} \sigma T^3 V. \tag{52.19}$$

In concluding this section a few observations should be passed on the problem of finding the volume of an elementary cell. It has already been shown that for a photon gas radiation the phase volume of a cell a must be assumed to be equal to h^3. In his work *Quantum Theory of a Monoatomic Ideal Gas* (1924), Einstein proposed to extend this result to ordinary particles with $m_0 \neq 0$, departing from de Broglie's idea that the wave-particle duality is inherent not only in radiation, but also in ordinary particles.

The phase volume of a cell was shown in Secs. 45, 46, 48 to be equal to h^3 for a six-dimensional μ-space of three translational degrees of freedom; h^2 for a four-dimensional μ-space of two rotational degrees of freedom; and h for a two-dimensional μ-space of vibrational degrees of freedom.

From this it follows that in the general case the phase volume of an elementary cell in an ideal gas, whose molecules have f degrees of freedom, equals h^f.

This conclusion is in accord with the quantum-mechanical uncertainty principle. It is common knowledge that the classical description of particle motion, using coordinates and momenta, although strictly speaking inadmissible in quantum mechanics, can be applied as an approximation if a coordinate and the corresponding momentum projection are determined simultaneously with the uncertainties Δx, $\Delta \xi$, related by the Heisenberg uncertainty rela-

tion

$$\Delta x\, \Delta \xi \geqslant h. \tag{52.20}$$

This signifies that in the optimal case, when there is a sign of equality in expression (52.20), the state is depicted in the phase plane (x, ξ) not by a point, but by a rectangle with an area $\Delta x\, \Delta \xi = h$.

The uncertainty relation is valid not only for Cartesian rectangular coordinates and momenta, but also for any canonically conjugated pairs of generalized coordinates and momenta for which the classical Poisson bracket is equal to unity. Therefore the state of any quantum-mechanical object with f degrees of freedom is described in a quasi-classical approximation not by a point in the $2f$-dimensional phase space, but by a cell with a volume h^f. In other words, we can consider the motion of a particle along classical trajectories in a phase space, but plot these trajectories in a way that one phase trajectory passes through each cell with a volume h^f.

The attention of the reader should be drawn to the following: the volume of a cell was shown in Sec. 45 to be equal to h^f, comparing the formulae derived upon subdivision of the μ-space into cells with precise quantum-mechanical formulae. It should be strongly emphasized, however, that to find the numerical value of a cell volume there is no need to turn to quantum-mechanical formulae. In fact, as has already been mentioned in Sec. 37, the internal energy of a gas of indistinguishable particles depends parametrically on a and the magnitude of a can be found by comparison with experiment, for instance, by measuring the constant σ present in the Stefan-Boltzmann law (as was done in this section) or by measuring the heat capacity of a Fermi gas (see Sec. 56).

This is of exceptional importance. It is indicative of the fact that the formal method of subdividing the μ-space of a gas into cells for the purpose of its statistical description, together with the hypothesis on particle indistinguishability, leads necessarily to the appearance in physics of a new universal constant, having the dimensionality of action. This constant h, whose numerical value was found by Planck in studying radiation laws, and by Einstein comparing his photo-effect formula with experimental data, could, unexpectedly, be found by measuring, for instance, the heat capacity of a boson or fermion gas. This means that the ideas of quantum mechanics, such as the indeterminacy principle, energy quantization, etc. are deeply rooted in statistical physics and that, as well as the two well-known roads to the discovery of quantum-mechanical ideas (the de Broglie-Schrödinger optical-mechanical analogy, and the Heisenberg-Born matrix model, based on the correspondence principle), there existed a third way. The fact that this way was not employed or its employment was delayed is a vivid illustration of historical accident.

Let us return now, in the light of the foregoing, to the statement of Pauli's exclusion principle given in Sec. 34. Like the use of the

concept of the μ-space of x, y, z, ξ, η, ζ and the identification of each discrete quantum state with a cell of phase volume a, this statement is seen to be admissible only in a quasi-classical approximation, which is known to be realized [7] by way of the limit transition $h \to 0$. It follows that in this approximation the cell volume is a small quantity and the phase volumes, playing an important part in this problem, must contain many cells.

The statement of the Pauli exclusion principle that makes no use of the concept of the μ-space is as follows: the probability that in a system of identical fermions two fermions have the same complete sets of quantum numbers is equal to zero.

Problem

At what temperature does the radiant energy density in a monoatomic gas become equal to the gas energy density?

Answer. $T = \left(\frac{3Nk}{2V\sigma}\right)^{1/3}$ K.

53. Thermal Motion in Crystals. Phonon Gas

The statistical theory of thermal motion in crystals bears a resemblance in many respects to the theory of equilibrium electromagnetic radiation, due to the fact that the thermal motion of atoms (ions, molecules) in a crystal lattice can be considered to a good approximation as a set of small (harmonic) oscillations. Since, due to the strong interaction, the oscillations of atoms are coupled, this means that the thermal motion in a crystal lattice is the superposition of normal lattice vibrations or of plane monochromatic waves with different frequencies ν and different directions of propagation.

In a crystal, however, waves differ considerably from electromagnetic waves in many respects. For one thing, the electromagnetic waves are of the transverse kind and they possess two independent polarization states. In contrast, in a crystal waves may be either of the transverse kind with two independent polarizations or of the longitudinal kind. In addition and of even greater importance, the set of electromagnetic waves is not limited in respect to frequency and there exist waves of any high frequency. For waves in a crystal the wavelength cannot be less than the minimum interatomic distance l, $\lambda_{\min} \approx l$, due to the lattice discreteness, and, consequently, the magnitude of frequency cannot exceed $\nu_{\max} \sim u/\lambda_{\min} \sim u/l$ (where u is the mean velocity of wave propagation). Therefore the total number of individual waves in a crystal is finite and determined by the number of vibrational degrees of freedom.

The total number of different oscillations is equal to $3N - 6$, since three translational and three rotational degrees of freedom of

a solid taken as a whole must be subtracted from the total number of degrees of freedom. Denoted by N is the total number of atoms or ions in a crystal, with atoms being considered as material points. Finally, it should be noted that for electromagnetic waves in a vacuum the law of dispersion, the relation between frequency ν and the wave vector f, has a simple form $\nu = \frac{cf}{2\pi}$, where the factor c is constant; the phase velocity is independent of frequency. In contrast to this, the law of dispersion, governing the behaviour of waves in a crystal, is generally of a more intricate form, since the propagation velocity of both transversal waves, u_t, and of longitudinal waves, u_l, depends on frequency.

Classical theory provides rather simple predictions for the internal energy and heat capacity of a solid. In accordance with the energy equipartition theorem, the contribution of each degree of freedom of vibrational motion to energy is equal to T. Thus, for one mole

$$U(T) = (3N_A - 6)\,T \approx 3N_A T \tag{53.1}$$

and, consequently,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N_A. \tag{53.2}$$

Formula (53.2) expresses the Dulong and Petit law which for a number of substances is well satisfied at room temperatures. For other solids, however, especially for very strong crystals built up of light atoms (for diamond, for instance), the Dulong and Petit law does not hold even at room temperatures, and at low temperatures the heat capacity of any crystal becomes significantly less than $3N_A$.

It should be noted that $3N_A$ is the classical value of heat capacity for atomic crystals. The number of ions per mole for ionic crystals equals nN_A, where n is the number of ions in an elementary crystal cell ($n = 2$ for NaCl, $n = 3$ for $CaCl_2$, etc.) and, according to classical theory, the heat capacity must be equal to $3nN_A$. As to molecular crystals (solid nitrogen, ice H_2O, etc.), for them the internal molecular heat capacity must be added to the lattice heat capacity due to the molecular rotational and vibrational degrees of freedom.

As in the case of equilibrium electromagnetic radiation, let us turn now to the corpuscular picture, in which normal oscillation (or, the same thing, each standing wave) is juxtaposed with a quantum oscillator having an energy $(N_i + 1/2)\,h\nu_i$, with the quantum numbers of each oscillator N_i being taken as the number of special quasi-particles, phonons, having an energy $\varepsilon_i = h\nu_i$ and a momentum $p_i = \frac{hf_i}{2\pi}$.

The term quasi-particle will also be encountered below in other problems (see Secs. 69, 70). This term is used to denote the excited

energy states of an ensemble of real particles corresponding to particular kinds of collective motions. In the case of phonons normal oscillations or elastic waves are involved*.

The concept of quasi-particle, in particular phonons, is a rather convenient means of mathematically describing a phenomenon. Just as for photons, the numbers of phonons in a cell are not limited and, consequently, phonons obey the Bose-Einstein distribution. The chemical potential of a phonon gas must then be assumed to be equal to zero, since, by analogy with the photon gas, the total number of phonons is not fixed; the phonons are continuously "absorbed" and "emitted" by a crystal lattice.

Let us write down the Bose-Einstein distribution and the expression for the internal energy of an ideal phonon gas (see Sec. 37):

$$N_i = \frac{1}{e^{h\nu_i/T} - 1}, \tag{53.3}$$

$$U = \sum_i g_i h\nu_i \left[\frac{1}{e^{h\nu_i/T} - 1} + \frac{1}{2} \right]. \tag{53.4}$$

It is clear that to calculate the internal energy, the frequency spectrum of a crystal lattice, ν_i, must be known, but its determination involves rather intricate calculations even for comparatively simple crystal lattices.

Debye calculated the internal energy and heat capacity of crystals with the aid of the so-called continuous model, referred to as the Debye model. This model presumes the dispersion law to be similar for a continuous medium and for electromagnetic radiations, i.e. the law is assumed to be linear. In accordance with this, the frequencies of longitudinal and transversal phonons are $\nu = \frac{fu_l}{2\pi}$ and $\nu = \frac{fu_t}{2\pi}$ respectively, where u_l and u_t are the propagation velocities for longitudinal and transversal elastic waves assumed to be independent of frequency. It should be noted that these expressions of frequency are obtained by expanding the function $\nu(f)$ in a series in powers of f and limiting the series to the first (linear) term. Therefore, strictly speaking, they are suitable only at small values of f (this is treated in greater detail at the end of the section).

Passing in formula (53.4) from summation to integration over

* It is known that upon transition to Cartesian coordinates the energy of a system of interacting particles is represented by the sum of independent terms pertaining to different normal oscillations (on the condition that in the expansion of the potential energy of particle interaction we limit ourselves to terms quadratic in displacements).

This means that upon passing to the corpuscular presentation of the quasi-particle gas, the quasi-particles (phonons) are non-interacting, and the phonon gas is an ideal one.

frequency ν, we obtain

$$U = \frac{12\pi hV}{u^3} \int_0^{\nu_{max}} \left[\frac{1}{e^{h\nu/T} - 1} + \frac{1}{2} \right] \nu^3 \, d\nu. \tag{53.5}$$

Expression (53.5) differs from (52.8) for the energy density of a photon gas (except the factor V) as follows.

1. The expression for U includes the term

$$U_0 = \frac{6\pi hV}{u^3} \int_0^{\nu_{max}} \nu^3 \, d\nu$$

representing the sum of the zero-point vibrational energies of oscillators.

2. Because there are three polarization states, and not two as is the case with photons, there is an extra factor $\frac{3}{2}$ in formula (53.5).

3. The factor c^{-3} is replaced in formula (53.5) by the factor $u^{-3} = \frac{1}{3}(u_l^{-3} + 2u_t^{-3})$, where u is the mean velocity of elastic wave propagation in a crystal.

4. The upper integration limit in formula (53.5) is equal to *Debye's frequency* ν_{max}, and it is not infinite as with photons. As has been already mentioned, the order of magnitude of the Debye frequency is equal to u/l, where l is the minimum interatomic distance in a lattice. Debye's theory specifies it more accurately by the relation

$$\frac{12\pi V}{u^3} \int_0^{\nu_{max}} \nu^2 \, d\nu = 3N - 6 \approx 3N,$$

with it being possible to calculate the number of oscillators in the frequency range between ν and $\nu + d\nu$ from formula (52.4) by introducing the additional factor $^3/_2$ and replacing c^3 by u^3. Then,

$$\nu_{max} = u \left(\frac{3N}{4\pi V} \right)^{1/3}. \tag{53.6}$$

We limit ourselves here to the consideration of simple crystals, containing one atom in an elementary cell. If the elementary cell contains n atoms (ions), N must be replaced by nN in all following relationships and formulae.

Let us introduce into formula (53.5) a new integration variable x with the aid of the relationship $h\nu/T = x$ and determine the characteristic temperature of crystals, or *Debye's temperature* θ by the

following formula:

$$\theta = h\nu_{max} = hu\left(\frac{3N}{4\pi V}\right)^{1/3}. \tag{53.7}$$

Expression (53.5) for the internal energy then reduces to

$$U = \frac{12\pi T^4 V}{h^3 u^3}\int_0^{\theta/T}\frac{x^3\,dx}{e^x-1} + N\varepsilon_0, \tag{53.8}$$

where $\varepsilon_0 = \frac{9}{8}h\nu_{max}$ is the zero oscillation energy.

Let us consider two limiting cases: $T/\theta \gg 1$ and $T/\theta \ll 1$.

At high temperatures $T \gg \theta$ we have $x < \theta/T \ll 1$ and, expanding the term e^x in the denominator into a series, we obtain

$$U = \frac{12\pi T^4 V}{h^3 u^3}\int_0^{\theta/T} x^2\,dx + N\varepsilon_0 \approx \frac{4\pi\theta^3}{h^3 u^3}VT. \tag{53.9}$$

Substituting the value of θ from (53.7), we obtain

$$U = 3NT, \quad C_V = 3N \tag{53.10}$$

in accordance with the Dulong-Petit law.

At low temperatures $T \ll \theta$ we have

$$\int_0^{\theta/T}\frac{x^3\,dx}{e^x-1} \approx \int_0^{\infty}\frac{x^3\,dx}{e^x-1} = \frac{\pi^4}{15} \tag{53.11}$$

[see Mathematical Appendix, formula (VII.2)], whence we find for the energy an expression similar to the Stefan-Boltzmann formula for the energy of luminous radiation:

$$U = \frac{4\pi^5 V}{15h^3u^3}T^4 + N\varepsilon_0, \tag{53.12}$$

and for the heat capacity

$$C_V = \frac{16\pi^5 V}{15h^3u^3}T^3. \tag{53.13}$$

This result is in a good agreement with experimental data*.

In the intermediate temperature interval the expression for the internal energy is of the form

$$U = 3NTD\left(\frac{\theta}{T}\right) + N\varepsilon_0 \tag{53.14}$$

* It is useful to note that the factor h^3 in the denominator of expression (53.13) represents the volume a of an elementary cell, which can also be determined by measuring the low-temperature heat capacity of a crystal.

and for the heat capacity

$$C_V = 3N\left[D\left(\frac{\theta}{T}\right) - \frac{\theta}{T}D'\left(\frac{\theta}{T}\right)\right], \tag{53.15}$$

where

$$D(y) = \frac{3}{y^3}\int_0^y \frac{x^3\,dx}{e^x - 1} \tag{53.16}$$

is the so-called *Debye function.*

It should be noted that the Debye formula is an interpolation formula which, strictly speaking, holds true only for $T \gg \theta$ and $T \ll \theta$. Actually, the assumption that the dispersion law can be described by $\nu = \frac{uf}{2\pi}$ is valid only for low frequencies, i.e. at long-wave oscillations. In these conditions a great number of atoms oscillate in almost one phase and the medium can be considered as a continuum. Therefore at low temperatures, when only low frequencies are of importance in the sum in formula (53.4), the Debye model is applicable. On the other hand, at very high temperatures all vibrational degrees of freedom are excited and make their "classical" contribution equal to T. The assumptions concerning frequency distribution are, therefore, unessential, and the Debye theory again provides good results. In the intermediate temperature range Debye's theory becomes approximate and is in adequate agreement with experiment only for the simplest crystals. To build up a theory, the crystal frequency spectrum or the dispersion equation must, in general, be known.

Expression (53.7) for the Debye temperature $\theta = h\nu_{max}$ indicates that the Debye temperatures are very high for strong crystals made up of light atoms and low for low-strength crystals build up of heavy atoms, since the characteristic frequencies are proportional to $\sqrt{\varkappa/m}$, where $\varkappa$ is the quasi-elastic constant, and m is the mass of atoms. Experimental results, for instance, are as follows: the Debye temperature θ is 1860 K for C (diamond), 1000 K for Be, 453 K for Fe, 215 K for Ag, 172 K for Na, 106 K for I and 88 K for Pb.

For this reason room temperatures are very high for substances such as Pb, I, Na and at these temperatures the Dulong and Petit law works well for them. By contrast, substances such as diamond, Be and others are associated with low room temperatures, at which the heat capacities of these solids obey the T^3 law.

Let us consider some problems associated with the dynamics of a crystal lattice. Only quadratic terms with respect to displacement are taken into account in the formula for the interaction energy of adjacent atoms (ions) in a small-amplitude vibration approximation. The motion of each atom is then the superposition of harmonic oscillations with frequencies ν_k. Let us represent the displacement

of an atom r (t) in the form

$$\mathbf{r}(t) = \sum_k \mathbf{a}(\nu_k)\, e^{2\pi i \nu_k t}; \tag{53.17}$$

the fact that r (t) should be real gives a $(\nu_k) = \mathbf{a}^* (-\nu_k)$.

In accordance with (53.17), the mean square displacement $\overline{r^2(t)}$ is

$$\overline{r^2(t)} = \sum_{k,\, l} \mathbf{a}(\nu_k)\, \mathbf{a}(\nu_l)\, \overline{\exp[2\pi i (\nu_k + \nu_l) t]} = \sum_k |\mathbf{a}(\nu_k)|^2, \tag{53.18}$$

since the mean value of the exponential for a large time interval, T, which can be assumed to be the greatest common multiple of periods ν_k^{-1}, equals δ_{kl}.

On the other hand, allowing for the fact that with harmonic oscillations the mean potential and the mean kinetic energies are the same, the mean energy of the selected atom is

$$\bar{E} = m\bar{\dot{r}}^2 = 4\pi^2 m \sum_{k,\, l} \mathbf{a}(\nu_k)\, \mathbf{a}(\nu_l)\, \nu_k \nu_l\, \overline{\exp[2\pi i (\nu_k + \nu_l) t]}$$

and, consequently,

$$\bar{E} = 4\pi^2 m \sum_k \nu_k^2 |a(\nu_k)|^2. \tag{53.19}$$

Due to the similarity of lattice atoms (for the sake of simplicity our discussion is limited to simple crystals with identical atoms), on the average the total energy is equal to

$$N\bar{E} = 4\pi^2 M \sum_k \nu_k^2 |a(\nu_k)|^2, \tag{53.20}$$

where M is the mass of a crystal.

Turning to a quantum-mechanical description, let us show the total energy of a crystal, expressed as the sum of the energies of harmonic oscillators with frequencies ν_k, equal to

$$4\pi^2 M \nu_k^2 |a(\nu_k)|^2 = \left(n(\nu_k) + \frac{1}{2}\right) h\nu_k = \left(\frac{1}{e^{h\nu_k/T} - 1} + \frac{1}{2}\right) h\nu_k, \tag{53.21}$$

where $n(\nu_k)$ is the number of phonons with frequency ν_k. It follows from Eq. (53.21) that

$$|a(\nu_k)|^2 = \frac{h}{4\pi^2 M \nu_k} \coth\left(\frac{h\nu_k}{2T}\right),$$

and, passing to integration over the Debye frequency spectrum, we find that the mean square displacement is equal to

$$\overline{r^2(t)} = \frac{3hV}{\pi M u^3} \int_0^{\nu_{\max}} \coth\left(\frac{h\nu}{2T}\right) \nu\, d\nu = \frac{3T^2}{\pi h \rho u^3} \int_0^{\theta/T} \coth\left(\frac{x}{2}\right) x\, dx, \tag{53.22}$$

where ρ is the crystal density.

In limiting cases we find:

1. $T \ll \theta$. According to formula (VII.2) in the Mathematical Appendix, we have

$$\int_0^{\theta/T} \coth\left(\frac{x}{2}\right) x\,dx \approx 2\int_0^{\infty} \frac{x\,dx}{e^x-1} + \frac{\theta^2}{2T^2} = \frac{\pi^2}{3} + \frac{1}{2}\left(\frac{\theta}{T}\right)^2,$$

whence

$$\overline{r^2} = \frac{3\theta^2}{2\pi h\rho u^3} + \frac{\pi T^2}{h\rho u^3}, \tag{53.23}$$

At $T \to 0$ the mean square displacement tends to the constant limit $\frac{3\theta^2}{2\pi h\rho u^3}$, due to the existence of zero-point oscillations.

2. $T \gg \theta$. Making use of the fact that for small values of x $\coth(x/2) \approx 2/x$, we obtain from formula (53.22)

$$\overline{r^2} = \frac{6\theta}{\pi h\rho u^3} T. \tag{53.24}$$

Expression (53.24) was used by Lindemann to derive an interesting semiempirical relation between the Debye temperature θ and the melting point. Let us assume that melting occurs at temperadure T_f, at which $\sqrt{\overline{r^2}}$ is a certain fraction ζ of the mean interatomic tistance. Then, using formula (53.24), we find

$$\frac{6\theta T_f}{\pi h\rho u^3} = \zeta^2 l^2, \quad T_f = \frac{\pi h\rho u^3 \zeta^2}{6\theta} l^2.$$

The parameter ζ has been shown experimentally to fall in the range 0.2 to 0.25 for most solids.

At high temperatures considerable atomic displacement takes place in a lattice and the effects of the anharmonicity of oscillations begin to play an important role which, in turn, leads to changes in the thermodynamic functions. In particular, the thermal expansion of crystalline solids can be reasonably explained only by taking into account the anharmonic terms in the expression for potential energy. To elucidate the physical meaning of this effect, let us take as a simple model a "chain" consisting of only two atoms.

First, let us assume the potential energy of interaction of atoms displaced over a distance $x = |\mathbf{r}_1 - \mathbf{r}_2| - l$ from the equilibrium position to be proportional to x^2, $\mathcal{U}(x) = m\omega^2 x^2/4$ (curve *1* in Fig. 71); then, due to the fact that the Boltzmann distribution function $e^{-\mathcal{U}(x)/T}$ is even, the mean displacement equals zero and is independent of temperature. It follows that the mean interatomic distances in a lattice are also independent of temperature, and so no thermal expansion occurs.

The real curve representing the potential energy of atomic interaction is asymetric (curve *2* in Fig. 71)—as the atoms draw closer together, the repulsive forces increase at a rate greater than that at which the attraction forces increase as atoms move away from each other. Consequently, with rising temperature and an increase in the oscillation amplitudes, the repulsive forces become more effective than the attraction forces and the mean interatomic distance increases. The asymmetry of the potential curve can be described to a first approximation by a correction proportional to x^3:

$$\mathcal{U}(x) = \frac{m\omega^2 x^2}{4} - \beta x^3.$$

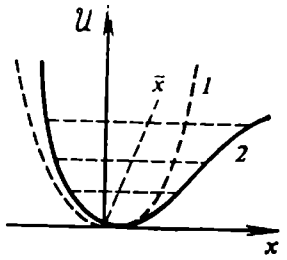


FIG. 71

The force of atomic interaction equals

$$F(x) = -\frac{\partial \mathcal{U}}{\partial x} = -\frac{m\omega^2 x}{2} + 3\beta x^2.$$

Assuming the mean force of interaction to be equal to zero in the state of mechanical equilibrium, we obtain

$$F(x) = -\frac{m\omega^2}{2}\bar{x} + 3\beta\bar{x}^2 = 0, \quad \bar{x} = \frac{6\beta\bar{x}^2}{m\omega^2}.$$

The mean square displacement in the above expression can be calculated in a harmonic approximation from the classical equipartition law $m\omega^2\bar{x}^2/4 = T/2$, whence we find that

$$\bar{x} = \frac{12\beta}{m^2\omega^4} T. \tag{53.25}$$

The mean interatomic distance depends on temperature linearly. The linear expansion coefficient $\alpha = \frac{1}{a+\bar{x}} \frac{d\bar{x}}{dT} \approx \frac{1}{a} \frac{d\bar{x}}{dT}$ is almost constant and equal to $\frac{12\beta}{m^2\omega^4 a}$.

Problems

1. Consider a two-dimensional crystal in Debye's approximation. Find its internal energy and heat capacity.

Answer. $U = \frac{4}{3} N\theta \left[1 + 3\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^2 dx}{e^x - 1}\right]$, $\theta = hu\left(\frac{N}{\pi\sigma}\right)^{1/2}$,

where σ is the crystal area.

2. Calculate the mean square atomic displacement for unidimensional and two-dimensional crystals. How can the apparent divergences be eliminated?
3. Assuming the Debye temperature to be a known function of volume, derive the equation of state for a Debye crystal

$$P = \left(\frac{U}{\theta} - \frac{9}{4}N\right)\frac{d\theta}{dV}.$$

What form does this equation acquire if the mean velocity u is assumed to be independent of volume? Consider the two limiting cases $T/\theta \gg 1$ and $T/\theta \ll 1$.

Answer. $P = \frac{3}{4}\frac{N\theta}{V} - \frac{1}{3}\frac{U}{V}$.

4. Derive the Grüneisen relation between the Grüneisen constant $\lambda = \frac{V}{\theta}\frac{d\theta}{dV}$, the isobaric thermal expansion coefficient $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, and the isothermal compressibility

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

Answer. $\alpha_P = \lambda K_T C_V/V$.

5. Show that for solid crystals the difference $C_P - C_V$ is small compared to the heat capacity C_P.

54. A Degenerate Bose Gas in the Absence of a Field. The Bose-Einstein Condensation

In Secs. 52, 53 we considered special cases of the Bose gas: the photon gas and the phonon gas. Let us consider now a monoatomic Bose gas in the absence of an applied field at low temperatures. Write down the formula for the Bose-Einstein distribution

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/T} - 1} \tag{54.1}$$

and the expressions for the total number of particles and the internal energy

$$N = \sum_i \frac{g_i}{e^{(\varepsilon_i - \mu)/T} - 1}, \tag{54.2}$$

$$U = \sum_i \frac{g_i \varepsilon_i}{e^{(\varepsilon_i - \mu)/T} - 1}. \tag{54.3}$$

It should be noted in the first place that the chemical potential of a Bose gas cannot be positive, since at $\mu > 0$ the number of particles

occupying the ground level, $\varepsilon_0 = 0$, and all levels satisfying the condition $\varepsilon_i < \mu$, would be negative: $e^{(\varepsilon_i - \mu)/T} < 1$. With diminishing temperature, the chemical potential μ, remaining negative, increases. In fact, differentiating Eq. (54.2) over T, we get

$$\mu'(T) = -T^{-1} \sum_i' \frac{g_i (\varepsilon_i - \mu) e^{(\varepsilon_i - \mu)/T}}{[e^{(\varepsilon_i - \mu)/T} - 1]^2} < 0.$$

The transition to integration in Eq. (54.2) should be made with some care. Although the distances between the energy levels for translational motion $\sim h^2/mL^2$ are always small compared to T (the characteristic temperature for translational motion $T_t \approx 0$, Sec. 45), in dealing with a Bose gas the sum in Eq. (54.2) cannot be simply replaced by an integral. Indeed, the integral derived from the sum in Eq. (54.2), when passing to continuously varying energy ε, has the form

$$\int_0^\infty \frac{\rho(\varepsilon)\, d\varepsilon}{e^{(\varepsilon - \mu)/T} - 1}, \quad \text{where} \quad \rho(\varepsilon) = AV\varepsilon^{1/2} = 2\pi g \left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon^{1/2}. \qquad (54.4)$$

It can be readily seen that the ground level $\varepsilon_0 = 0$ contributes nothing to the integral at low temperatures. In fact, when passing to integration, the first term in the sum in Eq. (54.2) must be replaced by the integral $AV \int_0^{\varepsilon'} d\varepsilon\, \varepsilon^{1/2} (e^{(\varepsilon - \mu)/T} - 1)^{-1}$, where ε' lies between $\varepsilon_0 = 0$ and $\varepsilon_1 \sim \frac{h^2}{mL^2}$. It will be shown below that at low temperatures $|\mu|/T$ is a macroscopically small quantity of the order of N^{-1}. The order of magnitude of the contribution of the level $\varepsilon_0 = 0$ is, therefore, $AVT^{3/2} \int_0^{\varepsilon' T} dx\, x^{1/2} (e^x - 1)^{-1}$ tending to zero together with T.

Meanwhile at low temperatures bosons must accumulate at the level $\varepsilon_0 = 0$, since at low temperatures all N_i, except N_0, decrease exponentially and their sum $\sum_{i \neq 0} N_i$, which can be replaced with a good degree of accuracy by the integral (54.4), also tends to zero. In accordance with the normalization condition, this means that at such temperatures the number of particles occupying the ground level must be of the order of N; then $g_0 (e^{-\mu/T} - 1) \sim N$, $\mu \sim -g_0 T/N$. At the thermodynamic limit, however, this implies that $\mu \to -0$ and we arrive at the conclusion that there must exist a range of sufficiently low temperatures $0 < T < T_0$ at which the chemical potential must be assumed equal to zero in the macroscopical sense.

Passing to a quantitative treatment of the subject matter, let us single out in formula (54.2) the zero-level contribution and pass to the integration over the other levels. Formula (54.2) reduces to

$$N = \frac{g_0}{e^{-\mu/T}-1} + AV \int_0^\infty \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{(\varepsilon-\mu)/T}-1}. \tag{54.5}$$

The internal energy is determined only by particles with $\varepsilon > 0$, and, by passing to integration in formula (54.3), we obtain

$$U = AV \int_0^\infty \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{(\varepsilon-\mu)/T}-1}. \tag{54.6}$$

It should be noted that at any temperature above T_0 the first term in (54.5) is macroscopically small compared to the second term (their ratio is about N^{-1}), and should be ignored at the thermodynamic limit. The resulting equation

$$N = AV \int_0^\infty \frac{\varepsilon^{1/2}\, \partial\varepsilon}{e^{(\varepsilon-\mu)/T}-1} \tag{54.7}$$

can only be approximately solved with respect to the chemical potential μ, by numerical or graphical methods. At temperature T_0 the chemical potential become macroscopically small ($\sim N^{-1}$) and must be assumed to be equal to zero at the thermodynamic limit. Assuming in Eq. (54.7) that $\mu = 0$ and $T = T_0$, we obtain a formula for calculating T_0:

$$N = AV \int_0^\infty \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\varepsilon/T_0}-1} = AVT_0^{3/2} \int_0^\infty \frac{x^{1/2}\, dx}{e^x-1}, \tag{54.8}$$

whence we find that [see formula (VII.4), Mathematical Appendix]

$$T_0 = \left(\frac{N}{2.33AV}\right)^{2/3} = 0.084\,\frac{h^2}{m}\left(\frac{N}{V}\right)^{2/3}. \tag{54.9}$$

At $T < T_0$ the chemical potential of a Bose gas remains macroscopically small, i.e. equal to zero at the thermodynamic limit, and the number of particles occupying the ground level becomes macroscopically large, comparable to N. Now, at $\mu = 0$, expression (54.7) determines not the total number of particles, but the number of particles N^* with $\varepsilon > 0$,

$$N^* = AVT^{3/2} \int_0^\infty \frac{x^{1/2}\, dx}{e^x-1} = 2.33AVT^{3/2}, \tag{54.10}$$

and the difference $N - N^* = N_0$ gives the number of particles occupying the ground level $\varepsilon_0 = 0$. Thus, the limit temperature T_0 is that below which a macroscopic fraction of all particles begins to pass to the level $\varepsilon_0 = 0$. The expressions for N^* and N_0 can be rewritten with the aid of formulae (54.8) and (54.10) to read

$$\frac{N^*}{N} = \left(\frac{T}{T_0}\right)^{3/2}, \quad \frac{N_0}{N} = 1 - \left(\frac{T}{T_0}\right)^{3/2}. \tag{54.11}$$

As $T \to T_0$, $N_0 \to 0$, $N^* \to N$, and the energies of all particles are positive. With temperature decreasing below T_0 a macroscopic fraction of particles begins to pass to the ground level $\varepsilon_0 = 0$; as $T \to 0$, $N_0 \to N$, $N^* \to 0$, with all particles occupying the ground level. This phenomenon is referred to as the *Bose-Einstein condensation* and temperature T_0 is called the *condensation temperature*. It is clear, however, that in the absence of an external field the term "condensation" is used in a rather conditional sense, and we speak here about condensation in an energy (on the level $\varepsilon_0 = 0$) or in a momentum (on the level $p = 0$) space, and not in a real three-dimensional space. The totality of particles with $\varepsilon_0 = 0$ is called condensate, and particles with $\varepsilon > 0$ are referred to as overcondensate particles.

Let us find the internal energy of a Bose gas at $T \leqslant T_0$. Assuming $\mu = 0$, we obtain from formula (54.6)

$$U = AV \int_0^\infty \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{\varepsilon/T} - 1} = AVT^{5/2} \int_0^\infty \frac{x^{3/2}\, dx}{e^x - 1} = AVK_{3/2}T^{5/2};$$

making use of formula (VII.6) of Mathematical Appendix, we find

$$U = 1.78AVT^{5/2} = 31.6\,\frac{m^{3/2}T^{5/2}V}{h^3}. \tag{54.12}$$

Let us also find the heat capacity, entropy and pressure of the gas at $T \leqslant T_0$. Differentiating Eq. (54.12) for the internal energy with respect to temperature, we find

$$C_V = \frac{5}{2}\,\frac{U}{T} = 4.45AVT^{3/2} = 79\,\frac{m^{3/2}T^{3/2}V}{h^3}, \tag{54.13}$$

while formula (54.9) is used to obtain

$$C_V = 1.92N\left(\frac{T}{T_0}\right)^{3/2}. \tag{54.14}$$

To find the entropy and pressure, first let us determine the Ω-potential

$$\Omega = -\frac{2}{3}\,U = -1.15AVT^{5/2} = -21\,\frac{m^{3/2}T^{5/2}V}{h^3}, \tag{54.15}$$

whence

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{N, V} = -\frac{5}{2}\frac{\Omega}{T} = 52.5\frac{m^{3/2}T^{3/2}V}{h^3}. \qquad (54.16)$$

Comparing with formula (54.13), we obtain

$$S = \frac{2}{3}C_V = 1.28N\left(\frac{T}{T_0}\right)^{3/2}. \qquad (54.17)$$

Pressure is determined from the equation

$$P = -\frac{\Omega}{V} = 1.15AT^{5/2} = 21\frac{m^{3/2}}{h^3}T^{5/2}. \qquad (54.18)$$

Thus, the entropy and heat capacity of a Bose gas tend to zero as $T \to 0$ in accordance with the Nernst theorem, while its pressure is independent of volume. The Bose gas is similar in this respect to a saturated vapour. This similarity is attributable to the fact that in a state with $\varepsilon_0 = 0$ "condensed" atoms have no momentum and fail to contribute to pressure.

Let us examine now the temperature interval just above the condensation point, $0 < (T - T_0)/T_0 \ll 1$. In this temperature interval $N_0 = 0$ and $|\mu|/T \ll 1$. However, in the expression

$$N = AVT^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^{x+|\mu|/T}-1} \qquad (54.19)$$

it proves impossible to expand into a power series in the small parameter $|\mu|/T$, since the coefficient at $|\mu|/T$ in this expansion is a divergent integral $\int_0^\infty dx\, x^{1/2}e^x\,(e^x - 1)^{-2}$. This is indicative of the fact that the right-hand side of Eq. (54.19) is a non-analytic function of the parameter $|\mu|/T$.

Let us transform the integral in Eq. (54.19) in the following way:

$$\Lambda = \int_0^\infty \frac{x^{1/2}\,dx}{e^{x+|\mu|/T}-1} = \int_0^\infty \frac{e^{-x-|\mu|/T}x^{1/2}\,dx}{1-e^{-x-|\mu|/T}}$$

$$= \sum_{k=1}^\infty e^{k-|\mu|/T}\int_0^\infty e^{-kx}x^{1/2}\,dx$$

$$= \sum_{k=1}^\infty \frac{e^{-k|\mu|/T}}{k^{3/2}}\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}\sum_{k=1}^\infty \frac{e^{-k|\mu|/T}}{k^{3/2}}. \qquad (54.20)$$

The sum of the series in Eq. (54.20) is calculated by means of Euler's formula (see Sec. 46). Introducing $y = |\mu|/T \ll 1$ we get

$$\sum_{k=1}^{\infty} e^{-k\nu} k^{-3/2} = -\sum_{k=1}^{\infty} \frac{1-e^{k\nu}}{k^{3/2}} + \zeta\left(\frac{3}{2}\right)$$

$$= 2.612 - \int_1^{\infty} \frac{1-e^{-k\nu}}{k^{3/2}}\, dk - \frac{1}{2}(1-e^{-\nu})$$

$$- \frac{1}{4}\left[\left(\frac{3}{2}+y\right)e^{-\nu} - \frac{3}{2}\right] - \ldots . \qquad (54.21)$$

It can be readily seen that the non-integrand terms in (54.21) are made up of small quantities of the order y. The integral in this expression can be transformed in the following manner:

$$\int_1^{\infty} \frac{1-e^{-k\nu}}{k^{3/2}}\, dk = \sqrt{y}\left[\int_0^{\infty} \frac{1-e^{-z}}{z^{3/2}}\, dz - \int_0^{y} \frac{1-e^{-z}}{z^{3/2}}\, dz\right],$$

and, accurate to the first-order infinitesimals in y, we find

$$\int_1^{\infty} \frac{1-e^{-k\nu}}{k^{3/2}}\, dk = \sqrt{y}\int_0^{\infty} \frac{1-e^{-z}}{z^{3/2}}\, dz - 2y + O(y^2). \qquad (54.22)$$

The integral $\int_0^{\infty} \frac{1-e^{\alpha z}}{z^{3/2}}\, dz$ can readily be calculated by differentiating with respect to parameter α; it turns out to be equal to $2\sqrt{\pi\alpha}$. Assuming $\alpha = 1$ and substituting the result into formulae (54.22), (54.21) and (54.20), we obtain

$$\Lambda = \frac{\sqrt{\pi}}{2}\left[2.612 - 2\sqrt{\frac{\pi|\mu|}{T}} + O\left(\frac{|\mu|}{T}\right)\right].$$

Equation (54.19) acquires the form

$$N = AVT^{3/2}\left[1.306 - \pi\sqrt{\frac{|\mu|}{T}}\right],$$

whence, allowing for formula (54.9), we obtain for the chemical potential in this temperature interval

$$\mu = -0.54T\left[1 - \left(\frac{T_0}{T}\right)^{3/2}\right]^2. \qquad (54.23)$$

Differentiating Eq. (54.23) with respect to temperature, we find that in the temperature interval under consideration $0 <$

$< (T - T_0)/T_0 \ll 1$,

$$\mu'(T) = -0.54\left[1-\left(\frac{T_0}{T}\right)^{3/2}\right]\left[1+2\left(\frac{T_0}{T}\right)^{3/2}\right],$$

$$\mu''(T) = -\frac{0.81}{T}\left\{3\left(\frac{T_0}{T}\right)^3 - \left[1-\left(\frac{T_0}{T}\right)^{3/2}\right]\left(\frac{T_0}{T}\right)^{3/2}\right\}.$$

Since at $T < T_0$, at the thermodynamic limit, the chemical potential must be considered to be identically equal to zero together with all its derivatives (Fig. 72), we arrive at the conclusion that at the point of condensation the chemical potential proper and its first derivative vary continuously, $\mu(T_0 + 0) = \mu(T_0 - 0) = 0$ and $\mu'(T_0 + 0) = \mu'(T_0 - 0) = 0$, and the second derivative $\mu''(T)$ undergoes a discontinuity jump

$$|\mu''|_{T_0} = \mu''(T_0+0) - \mu''(T_0-0) = -\frac{2.43}{T_0}. \qquad (54.24)$$

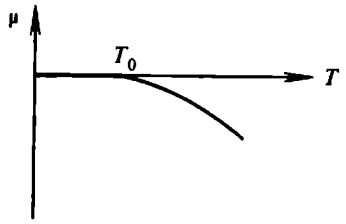


FIG. 72

The graph depicted in Fig. 72 approaches the T-axis at the point $T = T_0$, having a horizontal tangent and changing at that point only its curvature.

Let us now examine the nature of the phase transition occurring at the point $T = T_0$. According to formula (54.6), the internal energy varies continuously at the point $T = T_0$, since the function $\mu(T)$ tends to zero both as $T \to T_0 + 0$ and as $T \to T_0 - 0$.

Differentiating Eq. (54.6) with respect to T, we obtain for heat capacity C_V the expression

$$C_V = \frac{AV}{T}\int_0^\infty \frac{\varepsilon^{3/2} e^{(\varepsilon-\mu)/T}\left(\frac{\varepsilon-\mu}{T} + \mu'\right) d\varepsilon}{(e^{(\varepsilon-\mu)/T}-1)^2}, \qquad (54.25)$$

from which it follows [inasmuch as $\mu(T_0 + 0) = 0$ and $\mu'(T_0+0) = 0$] that there is no discontinuity jump in the heat capacity at the point $T = T_0$. Finally, differentiating Eq. (54.25) with respect to temperature, the derivative $\frac{\partial C_V}{\partial T}$ is found to have at the point $T = T_0$ a discontinuity jump equal to

$$\left(\frac{\partial C_V}{\partial T}\right)_{T_0} = \frac{AV\mu_0''}{T_0}\int_0^\infty \frac{\varepsilon^{3/2} e^{\varepsilon/T_0}\, d\varepsilon}{(e^{\varepsilon/T_0}-1)^2} = VAT_0^{3/2}\mu_0''\int_0^\infty \frac{x^{3/2}e^x\, dx}{(e^x-1)^2}.$$

Making use of expression (54.24), formula (VII.7) in the Mathematical Appendix and expression (54.9) for T_0, we find

$$\left(\frac{\partial C_V}{\partial T}\right)_{T_0} = -\frac{3.66N}{T_0}. \tag{54.26}$$

Thus, the Bose-Einstein condensation for a gas of free bosons is a third-order phase transition.

It should be noted that a somewhat different viewpoint is possible [10]. If the particles occupying the level with $\varepsilon_0 = 0$ and those on levels $\varepsilon > 0$ are regarded as two different "phases", then condensation must be seen as a first-order phase transition, since condensation is accompanied by a discontinuity jump in internal energy and entropy (the internal energy and entropy of the condensed phase are equal to zero). Such an interpretation requires, however, another definition of the phase, since phases are spatially separated in conventional first-order phase transitions, whereas no such separation exists in the case of the Bose-Einstein condensation in a gas of free bosons. In this connection the classification of the Bose-Einstein condensation either as a first- or third-order phase transition is purely terminological.

In reality, it proves impossible to observe the Bose-Einstein condensation, since at temperatures considerably higher than T_0 any Bose gas crystallizes, with the exception of helium. It is interesting to note, however, that He_2^4, the only Bose liquid existing at temperatures close to absolute zero, undergoes at the temperature 2.19 K a phase transition to the superfluid state. This temperature is close to temperature T_0 calculated by formula (54.9), ignoring molecular interaction. We shall consider in Sec. 69 the approximate theory of a non-ideal Bose gas, showing that the theory actually leads to superfluidity.

Emphasis should be laid on the different behaviour of a Bose gas and a gas consisting of classical Boltzmann particles at low temperatures. The Pauli exclusion principle is not valid for either of the gases, and for this reason, as the temperature drops, the particles of the two gases must accumulate on the lower energy level $\varepsilon_0 = 0$. However, the proportion of particles of the classical gas occupying the zero level is equal to

$$\frac{g_0}{\sum_i g_i e^{-\varepsilon_i/T}} \approx \frac{g_0}{AVT^{3/2}\int_0^\infty x^{1/2}e^{-x}\,dx}.$$

As has already been repeatedly stressed, statistical thermodynamics is an asymptotic theory the conclusions of which are only valid at the thermodynamic limit $N \to \infty$ and $V \to \infty$. Therefore the proportion of particles determined by the above equation at any finite temperature must be considered as the zero-level proportion. In con-

trast to this, the proportion of particles in a Bose gas occupying the zero level is equal to $\frac{g_0}{N(e^{-\mu/T}-1)}$ and even for finite temperatures $T \leqslant T_0$ this proportion becomes macroscopically large, i.e. comparable to unity [to be more exact, as is seen from Eq. (54.11), its order of magnitude is equal to $1 - (T/T_0)^{3/2}$].

Thus, the Bose-Einstein condensation is a phenomenon typical of bosons*, associated with the particle indistinguishability principle and the special properties of the Bose-Einstein distribution, as seen in the polar nature of the term $g_0 (e^{-\mu/T} - 1)^{-1}$.

Problems

1. Plot the family of curves $\mu (N/V)$ at different fixed temperatures for a Bose gas.
2. Plot on a P-V diagram the isotherms and adiabats of a degenerate Bose gas. What happens to these curves at the limit $T \gg T_0$?
3. Plot the isobars and adiabats of a Bose gas on a T-V diagram. Consider the transition to a Maxwell-Boltzmann gas.

55. The Bose Gas in an External Field

The situation of the free bosons considered in the preceding section may vary considerably in the presence of an external field. It is clear from the physical viewpoint that with a dropping temperature ($T \to 0$ K) bosons must accumulate near points at which the potential $\mathcal{U}(x, y, z)$ has minimum values, due to which the Bose-Einstein condensation must acquire the properties of conventional condensation occurring in a three-dimensional space. Let us consider for the sake of simplicity a Bose gas in a unidimensional field $\mathcal{U}(z)$ defined in the half-space $0 \leqslant z < \infty$ and normalized by the condition $\mathcal{U}(0) = 0$. The formulae for the number of particles and the internal energy (see Sec. 37) must now be rewritten to read

$$N^* = \frac{4\pi\sigma}{h^3} \int\int \frac{p^2\, dp\, dz}{e^{(\varepsilon-\mu)/T}-1}, \quad U = \frac{4\pi\sigma}{h^3} \int\int \frac{\varepsilon p^2\, dp\, dz}{e^{(\varepsilon-\mu)/T}-1}, \qquad (55.1)$$

where $\varepsilon = \frac{p^2}{2m} + \mathcal{U}(z)$, $\sigma = \int\int dx\, dy$, and N^* is the total number of particles at $T \geqslant T_0$ and the number of particles for $\varepsilon > 0$ at $T \leqslant T_0$. Let us turn, in formulae (55.1), to integration over

* It should be noted that the Bose-Einstein condensation takes place only in a system with a fixed number of bosons ($N = \text{const}$). In photon and phonon gases the chemical potential is equal identically to zero and condensation does not occur at any temperature.

the variables ε and z. The transition Jacobian for the ε-z plane is

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_z = \sqrt{\frac{m}{2[\varepsilon - \mathcal{U}(z)]}},$$

and the quantities N^* and U are expressed by

$$N^* = \int_0^\infty \frac{\rho(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/T}-1}, \quad U = \int_0^\infty \frac{\varepsilon\rho(\varepsilon)\, d\varepsilon}{e^{(\varepsilon-\mu)/T}-1}, \tag{55.2}$$

where the density of states $\rho(\varepsilon)$ is no longer expressed by formula $AV\varepsilon^{1/2}$, which is valid in the absence of a field [see (54.4)] and equal to

$$\rho(\varepsilon) = B \int_0^{\widetilde{\mathcal{U}}(\varepsilon)} \sqrt{\varepsilon - \mathcal{U}(z)}\, dz, \tag{55.3}$$

where $\widetilde{\mathcal{U}}(\varepsilon)$ = a function inverse to $\mathcal{U}(z)$ and $B = 4\sqrt{2}\pi\sigma m^{3/2}h^{-3}$.

In the presence of a field the condensation temperature is specified by the condition $N^* = N$ at $\mu = 0$, $T = T_0$. It follows that

$$N = \int_0^\infty \frac{\rho(\varepsilon)\, d\varepsilon}{e^{\varepsilon/T_0}-1}.$$

From Eq. (55.2) we obtain for heat capacity C_V the following expression:

$$C_V = \frac{1}{T}\int_0^\infty \frac{\varepsilon e^{(\varepsilon-\mu)/T}\left(\frac{\varepsilon-\mu}{T}+\mu'\right)\rho(\varepsilon)\, d\varepsilon}{(e^{(\varepsilon-\mu)/T}-1)^2},$$

whence for a discontinuity jump experienced by heat capacity at $T = T_0$ we obtain

$$[C_V]_{T_0} = \frac{\mu'(T_0+0)}{T_0}\int_0^\infty \frac{\varepsilon\rho(\varepsilon)\, e^{\varepsilon/T_0}\, d\varepsilon}{(e^{\varepsilon/T_0}-1)^2}. \tag{55.4}$$

The quantity $\mu'(T_0+0)$ is found by differentiating N^* in Eq. (55.2) with respect to T at $T > T_0$ and passing to the limit $T \to T_0 + 0$:

$$\mu'(T_0+0) = -\lim_{\substack{T\to T_0\\ \mu\to 0}} \frac{\int_0^\infty \frac{(\varepsilon-\mu)\, e^{(\varepsilon-\mu)/T}\rho(\varepsilon)\, d\varepsilon}{(e^{(\varepsilon-\mu)/T}-1)^2}}{T\int_0^\infty \frac{e^{(\varepsilon-\mu)/T}\rho(\varepsilon)\, d\varepsilon}{(e^{(\varepsilon-\mu)/T}-1)^2}}. \tag{55.5}$$

Let us examine the problem of convergence of the integrals pertinent in formulae (55.4) and (55.5) at small values of ε. As can be seen from Eq. (55.3), only small values of z are essential at small values of ε. Assume that at small z the potential $\mathcal{U}(z)$ tends to zero as z^n $(n > 0)$, i.e. $\mathcal{U}(z) \approx az^n$. Then, $\overline{\mathcal{U}}(\varepsilon) \approx (\varepsilon/a)^{1/n}$ and using formula (55.3) we find that

$$\rho(\varepsilon) \approx B \int_0^{(\varepsilon/a)^{1/n}} (\varepsilon - az^n)^{1/2}\, dz.$$

It follows that at small values of ε the density of states is of the order $\varepsilon^{1/2+1/n}$. The integrals on the right-hand side of Eq. (55.4) and in the numerator of (55.5) converge at any n (the order of magnitude of the integrand is $\varepsilon^{1/n-1/2}$ as $\varepsilon \to 0$, $\mu \to 0$). The order of magnitude of the integrand in the denominator of (55.5) is $\varepsilon^{-3/2+1/n}$, and the integral converges at $n < 2$. For such potentials $\mu_0'(T_0 + 0) \neq 0$ there exists a discontinuity jump in heat capacity at the point of the Bose condensation, and we are dealing with a second-order phase transition.

For potentials, decreasing for $z \to 0$ as z^2 or at a greater rate, the phase transition as $T \to T_0$ remains a third-order phase transition, just as for a gas of free bosons. Calculating the discontinuity jump $\left(\frac{\partial C_V}{\partial T}\right)_V$ at the condensation point [11] shows this jump to be infinite. In this respect a free boson gas $(n \to \infty)$ is an exceptional case associated with a finite discontinuity jump $\left(\frac{\partial C_V}{\partial T}\right)_V$.

Let us consider the spatial distribution of Bose-gas particles in the presence of a field $\mathcal{U}(z)$. The density of particles at $\varepsilon > 0$ can be found from formula (55.1) for N^*, if the integration over z is not applied to this formula. Passing to integration over the dimensionless kinetic energy $x = \frac{p^2}{2mT}$, we obtain

$$n^*(z) = \frac{dN^*}{\sigma\, dz} = \frac{4\pi \sqrt{2}\, m^{3/2} T^{3/2}}{h^3} \int_0^\infty \frac{x^{1/2}\, dx}{e^{x-\mu/T} - 1}$$

$$= 2\left(\frac{2\pi mT}{h^2}\right)^{3/2} \sum_{k=0}^{\infty} \frac{e^{k[\mu - \mathcal{U}(z)]/T}}{k^{3/2}}$$

[see the derivation of formula (54.20)], which leads to a more or less smooth dependence of n^* on z. At $T < T_0$, in addition to n^*, the term $n_0(z)$ appears, equal to the density of condensate particles and expressed by

$$n_0(z) = N_0 \delta(z) = (N - N^*)\, \delta(z),$$

since the condensate is formed by the particles with $p = 0$ and $z = 0$. This result is, however, very approximate, since as the par-

ticle density increases, an ever greater importance is assumed by, firstly, the quantum-mechanical effects, limiting the possibility of such an increase in density and associated with the uncertainty relations, and, secondly, the presence of repulsive forces between the particles, making the gas non-ideal. The rather intricate problems involved in the behaviour of a non-ideal Bose gas in an external field have not yet been solved. Some increase in the particle density in the vicinity of the minimum potential can, however, be expected to occur even when the forces of interaction (repulsion) are accounted for.

Problems

1. A Bose gas is placed in a unidimensional field with a potential $\mathcal{U}(z) = \alpha z$. Find the condensation temperature and the discontinuity jump experienced by the heat capacity.

Answer. $T_0 = \left(\frac{0.084\alpha N}{B}\right)^{2/5}$, $[C_V]_{T_0} = -3.19N$.

2. Find the same for a gas placed in a field with a potential $\mathcal{U}(z) = \alpha z^2$. Also find the discontinuity jump in the quantity $\frac{\partial C_V}{\partial T}$.

Answer. $T_0 = 2\left(\frac{6N}{\pi^3 B}\right)^{1/2}\alpha^{1/4}$, $B = \frac{4\sqrt{2}\,\pi\sigma m^{3/2}}{h^3}$,

$$[C_V]_{T_0} = 0, \quad \left(\frac{\partial C_V}{\partial T}\right)_{T_0} = \infty.$$

56. An Electron in a Periodic Field

This section is devoted to Fermi gases. Since many practical applications of theory, for instance, the properties of metals and semiconductors, are associated with the behaviour of a Fermi gas in crystal lattices, some quantum-mechanical ideas required in this connection will be treated briefly in this section (for greater detail see [12], [13]).

Ignoring in a zero-order approximation the oscillations of ions of a crystal lattice, we must consider the motion of electrons in a space-periodic field which is characterized by three noncoplanar vectors $\mathbf{a}_i$ ($i = 1, 2, 3$) determining the position of a fixed site of neighbouring cells with respect to a similar fixed site of the cell chosen primary. For a simple cubic lattice, for instance, the vectors $\mathbf{a}_i$ are orthogonal and equal modulo to the lattice constant a. The position of any fixed site of the lattice is then given by the vector $\mathbf{l} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where n_1, n_2, n_3 are integers. The lattice is assumed to be infinite, which removes the need to take boundary effects into consideration.

The potential energy is invariant upon translation by any lattice vector $\mathbf{l}$, $\mathcal{U}(\mathbf{r}+\mathbf{l}) = \mathcal{U}(\mathbf{r})$. We use for this problem the Schrödinger equation

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + E - \mathcal{U}(\mathbf{r})\right\}\psi(\mathbf{r}) = 0. \tag{56.1}$$

Due to the invariance of $\mathcal{U}(\mathbf{r})$ with respect to translations by vectors $\mathbf{a}_l$, the *Bloch theorem* is valid: the solution of Eq. (56.1) is

$$\psi(\mathbf{r}) = u_{\mathbf{p}}(\mathbf{r})\, e^{i\mathbf{p}\mathbf{r}}, \tag{56.2}$$

where $u_{\mathbf{p}}(\mathbf{r})$ is a periodic function, $u_{\mathbf{p}}(\mathbf{r}+\mathbf{l}) = u_{\mathbf{p}}(\mathbf{r})$.

The proof of the Bloch theorem is simple when the value of energy E is not degenerate. Due to the invariance of the Schrödinger equation (56.1), with respect to the translations by vectors $\mathbf{a}_l$ we have

$$\psi(\mathbf{r}+\mathbf{a}_l) = \lambda(\mathbf{a}_l)\,\psi(\mathbf{r}),$$

while according to the normalization condition $|\lambda(\mathbf{a}_l)| = 1$. Two translations by $\mathbf{a}_l$ and $\mathbf{a}_k$ result in the wave function being multiplied by $\lambda(\mathbf{a}_l)\,\lambda(\mathbf{a}_k)$, and the equality

$$\lambda(\mathbf{a}_l)\,\lambda(\mathbf{a}_k) = \lambda(\mathbf{a}_l + \mathbf{a}_k)$$

must be valid.

Allowing for the normalization condition, we find

$$\lambda(\mathbf{a}_l) = e^{i\mathbf{p}\mathbf{a}_l},$$

proving, thereby the validity of the Bloch theorem. When the level of energy E is degenerate, the Bloch theorem remains valid and can be proved by expanding the functions $\psi_k(\mathbf{r}+\mathbf{a}_l)$ in a system of orthonormalized functions $\psi_l(\mathbf{r})$ $(k,\ l = 1, 2, \ldots, g_E)$, where g_E is the degeneracy for level E, with subsequent diagonalization of the unitary matrix of this transformation $\psi_l(\mathbf{r}+\mathbf{a}_l) = C_{lk}^{(l)}\psi_k(\mathbf{r})$ (see the problem to this section).

The vector $\mathbf{p}$ in Eq. (56.2) is referred to as the *quasi-momentum* and can be determined accurate to the term $\mathbf{K}$, such that for any translation by the lattice vector $\mathbf{l}$ the equality

$$e^{i\mathbf{K}\mathbf{l}} = 1, \quad \mathbf{K}\mathbf{l} = L\cdot 2\pi$$

holds (L is an integer). The quasi-momentum can, however, be made uniquely determined by choosing as $\mathbf{p}$, for instance, the shortest vector out of the vectors $\mathbf{p}+\mathbf{K}$.

The function $u_{\mathbf{p}}(\mathbf{r})$ satisfies the condition

$$\left[\frac{\hbar^2}{2m}(\nabla - i\mathbf{p})^2 + E - \mathcal{U}(\mathbf{r})\right]u_{\mathbf{p}}(\mathbf{r}) = 0. \tag{56.3}$$

Equation (56.3) usually has several solutions $u_{\mathbf{p}l}(\mathbf{r})$, corresponding to the energies $E_l(\mathbf{p})$. The dependence $E_l = E_l(\mathbf{p})$ is called the

dispersion equation. The fact that in many cases, depending on the kind of a periodic field, the admissible values of E_i (p) and E_{i+1} (p) do not overlap is of paramount importance. This means that in the case of a periodic field the energy spectrum consists of a number of alternating zones of allowed energy values, separated by zones of forbidden energy levels. The energy E_i (p) is a function of the quasi-momentum projection within the limits of each zone. If the number of electrons is small and the temperature is not very high, the energy of most of the electrons is close to the minimum value of E_i (p). It is possible, then, to expand E_i (p) into a Taylor series in p_α and limit ourselves to the quadratic terms of the expansion, taking the bottom of a zone as reference point:

$$E_i(\mathbf{p}) = \frac{1}{2}\frac{\partial^2 E_i}{\partial p_\alpha \partial p_\beta} p_\alpha p_\beta = \frac{1}{2}(m_i^{-1})_{\alpha\beta} p_\alpha p_\beta \qquad (56.4)$$

(summation is performed over α and β).

The tensor $(m_i^{-1})_{\alpha\beta}$ is called the *tensor of inverse effective mass.* In the isotropic model $(m_i^{-1})_{\alpha\beta} = m_i^{-1}\delta_{\alpha\beta}$, in particular, formula (56.4) acquires the form $E_i(p) = \frac{p^2}{2m_i}$, similar to the expression for the kinetic energy of free particles. The quantity m_i is called the effective mass for the ith zone. It should be emphasized that m_i does not coincide with the true mass of particles and it can even be negative.

Problems

1. Extend the proof of the Bloch theorem to cover degenerate levels.
2. Consider an electron placed in a unidimensional periodic field consisting of a number δ-like equidistant wells (the Kronig-Penney model) $\mathcal{U}(x) = -\sum_{n=-\infty}^{\infty} \mathcal{U}_0 \delta(x - na)$. Find
   (a) the relationship between the quasi-momentum p and wave vector $k = -\left(\frac{2mE}{\hbar^2}\right)^{1/2}$;
   (b) the equation for allowed zones; (c) the dispersion equation for $ka \ll 1$*.

Answer. (a) $\cos pa = \cosh ka - \varkappa \sinh \frac{ka}{2k}$;

(b) $\cosh\left[ka - \operatorname{artanh}\left(\frac{\varkappa}{2k}\right)\right] < \left(1 - \frac{\varkappa^2}{4k^2}\right)^{-1/2}$;

(c) $E = \frac{\hbar^2}{ma^2}\left(1 - \frac{\varkappa a}{2} - \cos pa\right)\left(1 - \frac{\varkappa a}{6}\right)^{-1}$, $\varkappa = \frac{m\mathcal{U}_0}{\hbar^2}$.

* This problem was suggested by G. L. Kotkin.

57. Degenerate Fermi Gas. Electron Gas in Metals

In this section we deal with a gas of free fermions confined in a vessel of volume V. The application of this model to the practical case of an electron gas in a metal is based on two assumptions.

Firstly, the number of electrons in the lower energy zone is assumed to be less than one half of the number of levels, so that electrons can acquire energy, passing to higher levels in the same zone (the higher zones are separated from the lower zone by an energy interval, greater as compared to T, and they are not dealt with here). Secondly, the treatment is carried out within the framework of an isotropic model, so that the energy of particles is assumed to be equal to $\varepsilon = \frac{p^2}{2m}$, where m is the effective mass, which for electrons in a metal differs only slightly from their true mass.

Let us first consider a Fermi gas at absolute zero—a completely degenerate Fermi gas.

Consider the behaviour of the Fermi multiplier $f(\varepsilon) = (e^{(\varepsilon-\mu)/T} + 1)^{-1}$ as $T \to 0$:

$$\lim_{T\to 0} (e^{(\varepsilon-\mu)/T}+1)^{-1} = \sigma(\mu_0-\varepsilon) = \begin{cases} 1 \text{ at } \varepsilon < \mu_0, \\ 0 \text{ at } \varepsilon > \mu_0. \end{cases} \tag{57.1}$$

The quantity $\mu_0 = \mu\ (T = 0)$ in formula (57.1) is the limiting value of the chemical potential at $T \to 0$, while the term $\sigma(x)$ is a step function [see Mathematical Appendix, formula (VIII.5)].

The Fermi-Dirac distribution, described in Sec. 37,

$$N_i = g_i f(\varepsilon_i) = \frac{g_i}{e^{(\varepsilon_i-\mu)/T}+1}, \tag{57.2}$$

acquires at $T \to 0$ the form

$$\frac{N_i}{g_i} = \sigma(\mu_0-\varepsilon_i) = \begin{cases} 1 \text{ at } \varepsilon_i < \mu_0, \\ 0 \text{ at } \varepsilon_i > \mu_0, \end{cases} \tag{57.3}$$

as illustrated graphically in Fig. 73.

The physical meaning of formula (57.3) is clear. At $T = 0$ the fermions occupy the lowest energy levels. According to the Pauli exclusion principle, however, each state can be occupied by only one fermion; therefore the levels up to some maximum ε_{max} at $T = 0$ are occupied, with the occupation numbers per cell, N_i/g_i, being equal to unity for these levels and to zero for higher levels. As can be seen from Eq. (57.3), the maximum energy of fermions at $T = 0$, ε_{max}, referred to as the *Fermi energy*, coincides with the limiting value of the chemical potential μ_0.

In calculating thermodynamic quantities at $T = 0$, it should be noted that in the momentum space the fermions also occupy all

states with momenta ranging from zero to the maximum momentum p_{max}. In the momentum interval from p to $p + dp$, the number of quantum states equals $g \cdot 4\pi p^2 dp V h^{-3}$, where g is the spin degeneracy. Dealing with an electron gas, we assume $g = 2$. The number of electrons with momenta ranging from zero to the maximum momentum p_{max} is

$$N = \frac{8\pi V}{h^3} \int_0^{p_{max}} p^2 dp = \frac{8\pi V}{h^3} p_{max}^3. \tag{57.4}$$

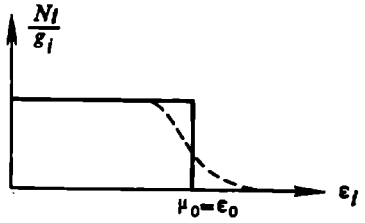


FIG. 73

It follows from the above that for the limit momentum, also referred to as the *Fermi momentum*, we have

$$p_{max} = \left(\frac{3N}{8\pi V}\right)^{1/3} h, \tag{57.5}$$

and for the Fermi energy ε_{max} we find the expression

$$\mu_0 = \varepsilon_{max} = \frac{p_{max}^2}{2m} = \left(\frac{3N}{8\pi V}\right)^{2/3} \frac{h^2}{2m}. \tag{57.6}$$

Finally, the total energy of a gas equals

$$U_0 = \frac{4\pi V}{mh^3} \int_0^{p_{max}} p^4 dp = \frac{4\pi V}{5mh^3} p_{max}^5; \tag{57.7}$$

substituting the value of p_{max} from (57.5), we find

$$U_0 = \frac{3}{5} N \varepsilon_{max}. \tag{57.8}$$

In compliance with the equation of state for ideal gases, $PV = \frac{2}{3} U$, we find the pressure of the Fermi gas at $T = 0$:

$$P_0 = \frac{1}{5} \left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{m} \left(\frac{N}{V}\right)^{5/3}. \tag{57.9}$$

Thus, the pressure of an electron gas differs from zero even at absolute zero temperature and, furthermore, it is rather high, compared to the pressure of an ideal classical gas at room temperatures, $P = NT/V$. Substitution of numerical values of $N/V \sim (10^{22}$ to $10^{23})$ cm^{-3} into formula (57.9) yields $P_0 \sim (10^4$ to $10^5)$ atm. It is clear that this stems from the fact that electrons are not at rest even at absolute zero tempeature, $T = 0$.

As can be seen from formula (57.8), at $T = 0$ the mean electron energy, equal to U/N, amounts to $\frac{3}{5} \varepsilon_{max}$ and the root-mean-square

velocity $\sqrt{\overline{v^2}}$ is equal to

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3}{5}}\frac{p_{max}}{m} = \sqrt{\frac{3}{5}}\left(\frac{3N}{8\pi V}\right)^{1/3}\frac{h}{m}.$$

Substituting numerical values into the above formula shows the order of magnitude of the root-mean-square velocity to fall within 10^7 to 10^8 cm/s.

All the formulae derived above are approximately applicable not only at $T = 0$, but also at sufficiently low temperatures. The validity condition for these formulae is, obviously, the smallness of the ratio T/μ. Indeed, at temperatures other than zero a number of electrons passes from levels below the Fermi boundary, $\varepsilon = \mu_0$, to levels above this boundary, resulting in the step shown in Fig. 73 turning into the dotted line depicted in the same figure. It can easily be seen from the Fermi-Dirac distribution (57.2) that the distribution half-width $\Delta\varepsilon \sim T$, and that for the above-derived formulae to be valid, the following inequalities should hold:

$$T \ll T_0 = \mu_0 = \varepsilon_{max},$$

where T_0 should be referred to as the degeneracy temperature of an electron gas (cf. Sec. 37). A numerical evaluation of the quantities ε_{max} and T_0 shows that $\varepsilon_{max} \sim 10^{-12}$ erg and $T_0 \sim (10^4$ to $10^5)$ K. It follows that an electron gas in metals remains degenerate at any temperature up to the fusion point.

For an electron gas the degeneracy condition can also be described by using expression (57.5) in the form

$$\frac{N}{V} \gg \frac{8\pi}{3}\left(\frac{2mT}{h^2}\right)^{3/2}. \qquad (57.10)$$

It should be realized that all the properties of a degenerate Fermi gas indicated above, the enormous internal pressure, high mean velocities, and high degeneracy temperature, are explained by the fact that the Fermi "step" in Fig. 73 is extremely "elongated" in the horizontal direction, if the distance between levels is taken as the unit energy.

Indeed, at low temperatures the number of occupied energy levels is proportional to $N/2$ and amounts to from 10^{22} to 10^{23} even for a piece of metal 1 cm^3 in volume. The ratio of the blurring width T to μ is clearly a fraction of the number of electrons involved in thermal motion, and it is rather small up to the metal melting point. This explains the well-known difficulty encountered by the classical theory of the heat capacity of metals based on the Maxwell-Boltzmann distribution.

If the conduction electrons in a metal are treated as a classical electron gas, then, in accordance with the energy equipartition law, these electrons must contribute additionally to the heat capacity.

their contribution being equal to $3N/2$. Actually, at room temperature the electron contribution to heat capacity is less than $3N/2$ by two orders of magnitude. Also, the electronic heat capacity C_e depends on temperature, or more exactly, C_e is directly proportional to T. The Maxwell-Boltzmann statistics fails to explain these facts; they can be understood only in terms of the Fermi-Dirac statistics.

The low heat capacity of an electron gas is explained qualitatively by the fact that at low temperatures $T \ll T_0$ only those electrons whose energy is close to the Fermi energy ε_{max} are engaged in thermal motion. Since these electrons constitute a small proportion, of the order of the ratio of the Fermi distribution blurring width $2T$ to μ_0, their contribution to the heat capacity is small, $C_e \sim \left(\frac{3}{2} N \frac{2T}{\mu_0}\right)$ and linearly depends on T.

Let us turn to a quantitative examination, departing again from the already known formulae

$$N = AV \int_0^\infty \frac{\varepsilon^{1/2}\, d\varepsilon}{e^{\varepsilon-\mu)/T}+1},$$

$$U = AV \int_0^\infty \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{(\varepsilon-\mu)/T}+1},$$

where for an electron gas $A = 4\pi\,(2m/h^2)^{3/2}$. It can be seen that at low temperatures $T \ll \mu_0$ the chemical potential can be eliminated from these formulae. In the Mathematical Appendix, AX, the integrals

$$M_n = \int_0^\infty \frac{\varepsilon^n\, d\varepsilon}{e^{(\varepsilon-\mu)/T}+1} \tag{57.11}$$

are evaluated on the condition that $T/\mu \ll 1$, and it is shown to the second order in (T/μ) that

$$M_n = \frac{\mu^{n+1}}{n+1}\left[1 + \frac{\pi^2 n\,(n+1)}{6}\left(\frac{T}{\mu}\right)^2\right]. \tag{57.12}$$

Then, the expression for N acquires the form

$$\frac{N}{AV} = M_{1/2} = \frac{2}{3}\,\mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{T}{\mu}\right)^2\right]. \tag{57.13}$$

Substituting the value of A, at $T = 0$ we find again

$$\mu_0 = \left(\frac{3N}{8\pi V}\right)^{2/3} \frac{h^2}{2m}.$$

With μ_0 Eq. (57.13) can be rewritten to read

$$\mu_0^{3/2} = \mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{T}{\mu}\right)^2\right].$$

In the small term $(\pi^2/8)\,(T/\mu)^2$ we can assume $\mu \approx \mu_0$; thus accurate to quantities $\sim (T/\mu_0)^2$, we obtain

$$\mu = \mu_0\left[1-\frac{\pi^2}{12}\left(\frac{T}{\mu_0}\right)^2\right]. \tag{57.14}$$

The expression for the internal energy is found dividing U by N (see p. 279)

$$\frac{U}{N}=\frac{M_{3/2}}{M_{1/2}}=\frac{3}{5}\mu\frac{1+\frac{5\pi^2}{8}\left(\frac{T}{\mu}\right)^2}{1+\frac{\pi^2}{8}\left(\frac{T}{\mu}\right)^2}\approx\frac{3}{5}\mu\left[1+\frac{\pi^2}{2}\left(\frac{T}{\mu}\right)^2\right] \tag{57.15}$$

and with the aid of formula (57.14), accurate to terms $\sim (T/\mu_0)^2$, we obtain

$$U=\frac{3}{5}N\mu_0\left[1+\frac{5\pi^2}{12}\left(\frac{T}{\mu_0}\right)^2\right]. \tag{57.16}$$

Hence, the heat capacity of an electronic gas is expressed by

$$C_e=\left(\frac{\partial U}{\partial T}\right)_{N,\,V}=\frac{\pi^2}{2}N\frac{T}{\mu_0}, \tag{57.17}$$

which is in compliance with experimental data and with the qualitative estimate made in the beginning of this section.

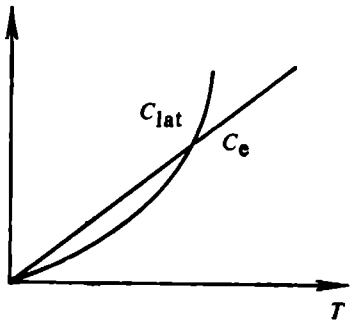


FIG. 74

It should be noted that although the electronic heat capacity is considerably less than the classical heat capacity $3N$ of a lattice, it even exceeds the lattice heat capacity at low enough temperatures, since in this region $C_{lat} \propto T^3$ (see Sec. 53), and $C_e \propto T$ (Fig. 74). Expression (57.17) includes implicitly the volume of an elementary cell [formula (57.6)] and, consequently, by measuring the heat capacity of an electron gas, it is possible to find this volume and show it to be equal to h^3.

To find the entropy and pressure of an electron gas, we determine the Ω-potential. According to (57.16) and (57.13),

$$\Omega=-\frac{2}{3}U=-\frac{2}{5}N\mu\left[1+\frac{\pi^2}{2}\left(\frac{T}{\mu_0}\right)^2\right]$$

$$=-\frac{4}{15}AV\mu^{5/2}\left[1+\frac{5\pi^2}{8}\left(\frac{T}{\mu_0}\right)^2\right], \tag{57.18}$$

whence the entropy of the gas is equal to

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = \frac{\pi^2}{3} AV\mu_0^{3/2}\frac{T}{\mu_0} = \frac{\pi^2}{2} N\frac{T}{\mu_0} \qquad (57.19)$$

to the second order in (T/μ_0). The entropy and heat capacity of an electron gas are seen to tend to zero as $T \to 0$ in accordance with the Nernst theorem.

The pressure of an electron gas is

$$P = -\frac{\Omega}{V} = \frac{2}{5}\frac{N\mu}{V}\left[1+\frac{\pi^2}{2}\left(\frac{T}{\mu_0}\right)^2\right]$$
$$= \frac{2}{5}\frac{N\mu_0}{V}\left[1+\frac{5\pi^2}{12}\left(\frac{T}{\mu_0}\right)^2\right] = P_0\left[1+\frac{5\pi^2}{12}\left(\frac{T}{\mu_0}\right)^2\right],$$

where P_0 is the pressure of a gas at $T = 0$, taken from formula (57.9).

A natural question may arise as to what extent is one justified in assuming the electron gas to be ideal and to ignore the interaction between particles at such high densities and pressures. Let us consider the electron gas against the background of a nuclei gas that compensates for the charge of the electron gas (the same as with metals and quasi-neutral plasma). The order of magnitude of the Coulomb interaction between electrons and nuclei related to one electron is Ze^2/a, where a, the mean spacing between electrons and nuclei, is approximately equal to $(ZV/N)^{1/3}$. For a non-degenerate electron gas the criterion of ideality would require the interaction energy to be small compared to the mean kinetic energy, whose order of magnitude is T, whence it follows that $N/V \ll \frac{T^3}{Z^3e^6}$, i.e. the criterion of ideality would be satisfied for a sufficiently rarefied gas. The order of magnitude of the mean kinetic energy of a heavily degenerate gas is $\mu_0 \propto \frac{h^2}{m}\left(\frac{N}{V}\right)^{2/3}$ it is proportional to a higher power of density N/V than the Coulomb energy. For this reason the criterion of ideality has the form

$$\frac{N}{V} \gg \gamma Z^2\left(\frac{me^2}{h^2}\right)^3 \qquad (57.20)$$

(γ is a numerical coefficient ranging approximately from 10^2 to 10^3), i.e. a degenerate electron gas is the more ideal the lower its density.

It can be readily verified that the criterion (57.20) is not satisfied for electrons in metals, therefore, agreement with the calculations made within the framework of the model of an ideal Fermi gas is rather approximate. The criterion of ideality is far better satisfied in some dense stars, the so-called white dwarfs. It should be noted that at a sufficiently high density an electron gas is not only an ideal

and degenerate gas, but also a relativistic one. For this to happen, the Fermi limit momentum must be comparable with mc. According to (57.5) we then obtain

$$\frac{N}{V} \geqslant \frac{8\pi}{3}\left(\frac{mc}{h}\right)^3 \sim 3 \times 10^{32}\ \text{cm}^{-3}. \qquad (57.21)$$

In this connection, a relativistic heavily degenerate electron gas often arises in astrophysical applications (see Problem 3 at the end of this section).

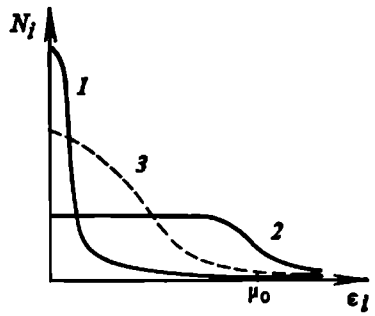


FIG. 75

In conclusion let us compare the diagrams representing the Bose-Einstein (*1*), Fermi-Dirac (*2*) and Maxwell-Boltzmann (*3*) distributions at low temperatures (Fig. 75). The Bose-Einstein distribution function has a sharp maximum at $\varepsilon = 0$—the Bose-Einstein condensation—and the function decreases exponentially with rising ε. The curve representing the Fermi-Dirac distribution has a flat plateau at $\varepsilon < \mu_0$, then runs downward, also exponentially. In the region of small occupation numbers both curves almost coincide with each other and with the curve depicting the Maxwell-Boltzmann distribution. The latter curve is plotted as a dotted line, indicating that it has meaning only in the region of small occupation numbers and high energies respectively.

Problems

1. Plot the isotherms and adiabats for a Fermi gas on a P-V plane.
2. Plot the isobars and adiabats for a Fermi gas on a T-V plane.
3. Find the internal energy and pressure of a completely degenerate ($T = 0$) ultrarelativistic Fermi gas.

Answer. $U = \frac{3}{8}\left(\frac{6}{g}\right)^{1/2} hcN\left(\frac{N}{V}\right)^{1/3}$, $P = \frac{1}{8}\left(\frac{6}{g}\right)^{1/2} hc\left(\frac{N}{V}\right)^{4/3}$.

4. Find the relationship between the equilibrium radius R and the mass M of a white dwarf, in which the main contribution to pressure is made by a completely degenerate electron (non-relativistic) gas.

Answer. $RM^{1/3} = \text{const}$.

58. Electrons in a Semiconductor

The electron energy spectrum in a pure semiconductor consists of a number of bands. The first, valence band, and the second, conduction band, are separated from each other by a gap whose width Δ is of the order of 0.5 to 3.0 eV. Higher bands are of no consequence to the physical phenomena associated with semiconductors and they will not be considered here. At absolute zero the energy levels of the lower band are fully occupied by electrons and the conduction band levels are free, so that the crystal has zero conductivity. With rising temperature a fraction of the electrons pass to energy levels in the conduction band and vacant places, "holes", form in the valence band. Acted upon by an electric field, the electrons in the upper band can now acquire energy and move in a direction opposite to the field, and the holes in the direction of the field. The crystal becomes a conductor and the conductivity, referred to as *intrinsic conductivity*, is the sum of the n- and p-type conductivities.

The idea of holes in the valence band can be described mathematically in the following manner. Let us write down the normalization condition for the total number of electrons,

$$N = \sum_i \frac{g_i}{e^{(\varepsilon_i - \mu)/T} + 1} + \sum_\alpha \frac{g_\alpha}{e^{(\varepsilon_\alpha - \mu)/T} + 1} = \sum_i g_i, \qquad (58.1)$$

where the subscript i denotes the levels in the valence band, and α the levels in the conduction band. The last equality in formula (58.1) follows from the fact that at absolute zero it is precisely the total number of electrons N that fills the valence zone (the Fermi level μ_0 will be shown below to lie in the forbidden band, i.e. above the valence band). Transferring the term $\sum_i \frac{g_i}{e^{(\varepsilon_i - \mu)/T} + 1}$ to the right-hand side of Eq. (58.1), we obtain

$$\sum_\alpha \frac{g_\alpha}{e^{(\varepsilon_\alpha - \mu)/T} + 1} = \sum_i g_i \left(1 - \frac{1}{e^{(\varepsilon_i - \mu)/T} + 1}\right) = \sum_i \frac{g_i}{e^{(\mu - \varepsilon_i)/T} + 1}. \qquad (58.2)$$

The number of holes in the valence band is on the right-hand side of formula (58.2), which expresses the *condition of electrical neutrality*: the number of electrons in the conduction band, n_e, is equal to the number of holes in the valence band, n_p. Passing to integration, we limit ourselves to a consideration of an isotropic model with a quadratic dispersion law. Then, the expressions for the number of electrons and the number of holes per unit volume and in the energy interval from ε to $\varepsilon + d\varepsilon$ can be rewritten to read

$$\frac{dn_e}{d\varepsilon_e} = A_e \frac{\varepsilon_e^{1/2}}{e^{(\varepsilon_e + \Delta - \mu)/T} + 1}, \quad \frac{dn_p}{d\varepsilon_p} = A_p \frac{\varepsilon_p^{1/2}}{e^{(\mu + \varepsilon_p)/T} + 1}, \qquad (58.3)$$

where $A_e = 4\pi \left(\frac{2m_e}{h^2}\right)^{3/2}$;

$$A_p = 4\pi \left(\frac{2m_p}{h^2}\right)^{3/2};$$

m_e and m_p = effective masses of electrons in the valence and in conduction bands respectively.

The readings of the energies ε_e and ε_p are taken from the bottom of the conduction band and the top of the valence band respectively [$\varepsilon_e + \Delta$ is the energy of an electron in the conduction band, the reading of which is taken, as with ε_p, from the top of the valence band (Fig. 76)].

The quantity $\frac{dn}{d\varepsilon}$ is plotted as a function of ε in Fig. 77, in which the dotted lines represent the densities of levels in the valence band $\varepsilon < 0$ and in the conduction band $\varepsilon > \Delta$, while the solid lines depict the electron densities in the two bands. The difference between

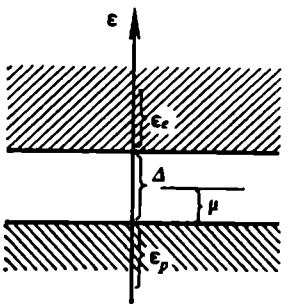


FIG. 76

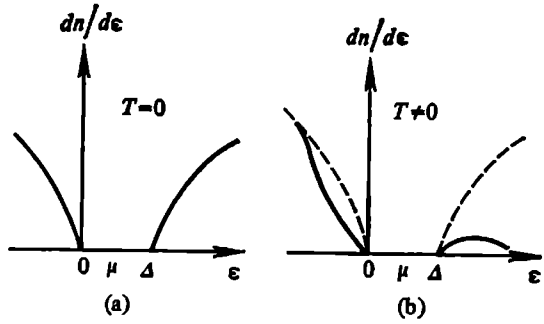


FIG. 77

the ordinates of the solid and dotted lines for the valence band yields the hole density. At $T = 0$ the two curves coincide and the number of holes is equal to zero (Fig. 77*a*). Integrating expressions (58.3), we obtain the total electron and hole densities, n_e and n_p. Due to the rapid convergence of the integrals, the upper limit of integration can be replaced by ∞.

Let us assume, in addition, that the two inequalities, $e^{(\Delta-\mu)/T} \gg 1$ and $e^{\mu/T} \gg 1$, permitting the Fermi-Dirac distribution function to be replaced by the Maxwell-Boltzmann exponential on the right-hand sides of Eq. (58.3), are valid. The two inequalities will be shown below to be equivalent and satisfied at any practically attainable temperatures. The physical explanation of this is that at any temperature up to the melting point the electron and hole occupation numbers are small compared to unity and, therefore, the electron gas and the gas of holes are not genenerate in the conduction and

valence bands respectively. Integrating expressions (58.3), we obtain

$$n_e = A_e e^{(\mu-\Delta)/T} \int_0^\infty e^{-\varepsilon/T} \varepsilon^{1/2}\, d\varepsilon = 2\left(\frac{2\pi m_e T}{h^2}\right)^{3/2} e^{(\mu-\Delta)/T}, \quad (58.4)$$

$$n_p = A_p e^{-\mu/T} \int_0^\infty e^{-\varepsilon/T} \varepsilon^{1/2}\, d\varepsilon = 2\left(\frac{2\pi m_p T}{h^2}\right)^{3/2} e^{-\mu/T}. \quad (58.5)$$

Making use of the condition of electrical neutrality, $n_e = n_p$, we find the chemical potential

$$\mu = \frac{\Delta}{2} + \frac{3}{4} T \ln\left(\frac{m_e}{m_p}\right). \quad (58.6)$$

Since the effective masses m_e and m_p are of the same order of magnitude, the second term in Eq. (58.6) is small compared to the first and the Fermi level is located in the middle of the forbidden band. The non-degeneracy conditions for the electron gas and the gas of holes, $e^{(\Delta-\mu)/T} \gg 1$ and $e^{\mu/T} \gg 1$, now coincide and lead to the inequality $e^{\Delta/2T} \gg 1$, which is satisfied up to $T \leqslant 10^3$ K.

Multiplying the expressions (58.4) and (58.5) and allowing for the condition $n_e = n_p$, we find

$$n_e = n_i = 2\left(\frac{2\pi m T}{h^2}\right)^{3/2} e^{-\Delta/2T},$$

where $m = (m_e m_p)^{1/2}$.

The internal energy, heat capacity and other thermodynamic functions of semiconductors can be readily calculated by the reader.

The properties of semiconductors change considerably in the presence of impurities. Two types of impurity atoms can be distinguished.

Donor atoms incorporate loosely bound electrons that through thermal motion can enter the conduction band and give rise to electron impurity conductivity.

Acceptor atoms easily capture an additional electron. If these electrons come from the valence band, holes appear in it giving rise to hole impurity conduction. *Impurity* (*extrinsic*) *conductivity* usually exceeds many times intrinsic conductivity in both cases. The properties of semiconductors with impurities are treated in greater detail in the special literature [12], [14].

It should be noted in conclusion that the simple picture of two bands separated by a gap $\Delta = \text{const}$ can be imagined only in a single-electron approximation. If electron interaction is taken into account, then, in the next approximation, the gap width becomes a function of density n. This significantly changes the thermodynamic properties of semiconductors and may lead in some models (see problem for Sec. 80) to "slamming" of the gap and the appearance of a phase transition in the metal state.

Problem

Find the electron-hole internal energy and the heat capacity of a pure semiconductor. Compare the latter with the heat capacity of a crystal lattice.

Answer. $U = 2\left(\frac{2\pi mT}{h^2}\right)^{3/2} e^{-\Delta/2T}(3T+\Delta)$,

$$C = 2\left(\frac{2\pi mT}{h^2}\right)^{3/2} e^{-\Delta/2T}\left[\frac{15}{2}+3\frac{\Delta}{T}+\frac{1}{2}\left(\frac{\Delta}{T}\right)^2\right].$$

59.* Magnetism of an Electron Gas

Let us consider an electron gas in a magnetic field with intensity H [15]. The presence of a field gives rise to two effects. One, the orientation of magnetic spin moments parallel to the field, has already been considered in Sec. 51 in the Maxwell-Boltzmann statistics approximation. For weak fields and high temperatures we find from formula (51.11) that

$$M = M_0\frac{\mu_B H}{T} = \chi H.$$

In addition, an electron gas possesses, however, a diamagnetic moment directed antiparallel to the external field. It should be noted in the first place that the diamagnetic effect is of a purely quantum origin and it does not exist in a classical electron gas, this following from the fact that the Lorentz force, acting on a particle in a magnetic field, $\mathbf{f} = \frac{e}{c}[\mathbf{v}, \mathbf{H}]$, is perpendicular to the direction of velocity and, consequently, performs no work on the particle. For this reason, if no allowance is made for the potential energy of spin $\mu_B H$, which leads to a paramagnetic effect, its energy is independent of the field and the magnetic moment $\mu = -\frac{\partial \varepsilon}{\partial H} = 0$.

However, it is different in the quantum-mechanical theory of magnetism, as was discovered by L. D. Landau in 1930. The fact is that in a permanent magnetic field a charge travels along helical lines the axes of which are parallel to the field. For this reason the motion of an electron parallel to the field is infinite and, consequently, nonquantized. But in the plane perpendicular to the field the electron moves in a circle with the Larmor frequency $\omega_L = eH/mc$ and the motion, being finite, is quantized.

The energy levels of an electron in a permanent magnetic field directed along the z-axis were shown by Landau [7] to be defined by the formula

$$\varepsilon(p_z, H) = \mu_B H(2n+1) + \frac{p_z^2}{2m} \pm \mu_B H \quad (n = 0, 1, 2, \ldots), \qquad (59.1)$$

where $\mu_B H(2n + 1)$ = quantized levels of the "transverse" fraction of the kinetic energy;

$\frac{p_z^2}{2m}$ = its non-quantized "longitudinal" fraction.

Due to quantization of the "transverse" energy, the kinetic energy of an electron is dependent on the intensity of the magnetic field. By virtue of the presence of the non-quantized fraction $\frac{p_z^2}{2m}$, the energy levels form a continuous energy spectrum and the number of states with a fixed n and a longitudinal moment in the interval $(p_z, p_z + dp_z)$ is equal to

$$\rho(p_z)\, dp_z = \frac{V}{h^3} \frac{eH}{c}\, dp_z.$$

Let us write down the expression for the Ω-potential of an electron gas in the following form:

$$\Omega(\mu, H, T) = -T \sum_{(q)} \ln\left(1 + e^{[\mu - \varepsilon(q)]/T}\right), \tag{59.2}$$

where the symbol (q) denotes the set of arguments p_z, n, s (spin) on which the energy depends, and the sign $\sum_{(q)}$ indicates that the summation is performed over n and over two directions of spin, while integration is performed over p_z:

$$\sum_{(q)} \ldots = \sum_{s} \sum_{n=0}^{\infty} \int dp_z \rho(p_z)$$

According to formula (38.19), the differential of $\Omega(\mu, H, T)$ is $d\Omega = -S\, dT - MV\, dH - N\, d\mu$, the latter expression allowing one to determine the number of particles, the magnetization M and the magnetic susceptibility $\chi = \frac{M}{H}$ with the aid of the formulae

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, H}, \quad M = -\frac{1}{V}\left(\frac{\partial \Omega}{\partial H}\right)_{T, \mu}, \quad \chi = -\frac{1}{VH}\left(\frac{\partial \Omega}{\partial H}\right)_{T, \mu}.$$

It should be noted that in using formula (59.1) for energy, we consider jointly both the diamagnetic [first term in Eq. (59.2)] and the paramagnetic ($\pm \mu_B H$) effects. It is difficult to perform a direct limit transition $T \to 0$ in expression (59.2), since the integrand undergoes a discontinuity jump at this limit.

For our purposes it is important to transform the sum (59.2) into some contour integral in the plane of an auxiliary complex argument λ, using formulae (XII.3), (XII.4) and (XII.5) of the Mathematical Appendix. Formula (XII.3) permits the reduction of expres-

sion (59.2) to

$$\Omega(\mu, H, T) = -\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{\pi\lambda T}{\sin \pi\lambda T} \frac{\sum\limits_{(q)} e^{\lambda[\mu-\varepsilon(q)]}}{\lambda^2}\, d\lambda,$$

and using formula (XII.4), we find that

$$\Omega(\mu, H, T) = -\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{d\lambda}{\lambda^2}\int_{-\infty}^{\infty} d\xi \frac{\sum\limits_{(q)} e^{\lambda[\xi T+\mu-\varepsilon(q)]}}{4\cosh^2(\xi/2)}. \quad (59.3)$$

Now it is easy to perform a limit transition $T \to 0$ in formula (59.3); integrating over ξ, we obtain

$$\Omega(\mu, H, 0) = -\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} d\lambda \frac{\sum\limits_{(q)} e^{\lambda[\mu-\varepsilon(q)]}}{\lambda^2}\int_{-\infty}^{\infty} \frac{d\xi}{4\cosh^2(\xi/2)}$$

$$= -\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} d\lambda \frac{\sum\limits_{(q)} e^{\lambda[\mu-\varepsilon(q)]}}{\lambda^2}. \quad (59.4)$$

Changing the integration sequence in formula (59.3) and taking account of formula (59.4) with the substitution $\mu \to \mu + \xi T$, we find

$$\Omega(\mu, H, T) = \int_{-\infty}^{\infty} d\xi \frac{\Omega(\mu+T\xi, H, 0)}{4\cosh^2(\xi/2)} = \frac{1}{T}\int_{-\infty}^{\infty} d\eta \frac{\Omega(\eta, H, 0)}{4\cosh^2(\eta-\mu/2T)}.$$

This suggests the following important property of the Ω-potential: at temperature T the dependence on μ is determined unambiguously by the dependence of Ω on μ at $T = 0$. It follows that a thermodynamic description of an electron gas requires a knowledge of $\Omega(\mu, H, T)$ at $T = 0$. According to formulae (59.4) and (XII.5) we have

$$\Omega(\mu, H, 0) = -\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} d\lambda \frac{\sum\limits_{(q)} e^{\lambda[\mu-\varepsilon(q)]}}{\lambda^2}$$

$$= -\sum_{(q)} [\mu - \varepsilon(q)]\, \sigma[\mu - \varepsilon(q)].$$

Let us first sum up in the above expression over n and over two spin directions. It is clear that the difference $\mu - \varepsilon$ for the quantum number $n - 1$ and the spin parallel to the field will be equal to the same

difference for n and the spin antiparallel to the field (for all values of n):

$$\mu-(2n-1)\,\mu_B H-\mu_B H-\frac{p_z^2}{2m}=\mu-(2n+1)\,\mu_B H+\mu_B H-\frac{p_z^2}{2m}$$

$$=\mu-2n\mu_B H-\frac{p_z^2}{2m}.$$

Owing to this all terms of the sums over n are doubled, except for the term with $n = 0$ and the spin antiparallel to the field, and we obtain

$$\Omega(\mu, H, 0)=-\frac{V}{h^2}\frac{eH}{c}\int\left[\mu-\frac{p_z^2}{2m}+2\sum_{n=1}^{\infty}\left(\mu-2n\mu_B H-\frac{p_z^2}{2m}\right)\right]dp_z.$$

On account of the factor $\sigma\left(\mu-2n\mu_B H-\frac{p_z^2}{2m}\right)$ omitted in the above expression, in each term of the sum integration is carried out over the interval between two zeros of the integrand from $-\sqrt{2m(\mu-2n\mu_B H)}$ to $+\sqrt{2m(\mu-2n\mu_B H)}$.

Upon integration, we find that within the interval $2l\mu_B H < \mu < (2l+1)\,\mu_B H$, where l is an integer, the values of μ are expressed by

$$-\Omega(\mu, H, 0)=N\mu_B H\left[\left(\frac{\mu}{\mu_0}\right)^{3/2}+2\sum_{n=1}^{l}\left(\frac{\mu-2n\mu_B H}{\mu_0}\right)^{3/2}\right], \quad (59.5)$$

where μ_0 denotes the chemical potential of an electron gas in the absence of a magnetic field and at temperature $T = 0$:

$$\mu_0=\left(\frac{3N}{8\pi V}\right)^{2/3}\left(\frac{h^2}{2m}\right).$$

For our purposes it is more convenient to rewrite expression (59.5) to read

$$-\Omega(\mu, H, 0)=N\mu_0\left(\frac{\mu_B H}{\mu_0}\right)^{5/2}\left[\left(\frac{\mu}{\mu_B H}\right)^{3/2}+2\sum_{n=1}^{l}\left(\frac{\mu}{\mu_B H}-2n\right)^{3/2}\right]. \quad (59.6)$$

Let us introduce the following notation:

$$x=\frac{\mu(H, 0)}{\mu_B H}, \quad R_a(x)=ax^{a-1}+2a\sum_{n=1}^{\infty}(x-2n)^{a-1}\sigma(x-2n). \quad (59.7)$$

Differentiating the expression for the function $R_a(x)$, we get

$$\frac{dR_a}{dx} = a\left[(a-1)\,x^{a-2} + 2(a-1)\sum_{n=1}^{\infty}(x-2n)^{a-2}\,\sigma(x-2n)\right] + 2a\sum_{n=1}^{\infty}(x-2n)^{a-1}\,\delta(x-2n),$$

where $\delta(x)$ is the Dirac delta function. From this it is clear that at any $a > 1$ the relationship $\frac{dR_a}{dx} = aR_{a-1}$ exists, but at $a \leqslant 1$ the derivative of the function $R_a(x)$ becomes infinity at $x = 2l$ (where l is an integer), and the function $R_a(x)$ undergoes discontinuity jumps at these points, which are finite at $a = 1$ and infinite at $a < 1$.

Substituting formula (59.7) into (59.6), we obtain

$$-\Omega(\mu, H, 0) = \frac{2}{5} N\mu_0 \left(\frac{\mu_B H}{\mu_0}\right)^{5/2} R_{5/2}(x),$$

whence we find

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,H} = N\left(\frac{\mu_B H}{\mu_0}\right)^{3/2} R_{3/2}(x), \tag{59.8}$$

$$\chi(H, 0) = -\frac{1}{VH}\left(\frac{\partial\Omega}{\partial H}\right)_{\mu, T} = \frac{N}{V}\frac{\mu_B^2}{\mu_0}\left(\frac{\mu_B H}{\mu_0}\right)^{1/2}[R_{5/2}(x) - xR_{3/2}(x)]. \tag{59.9}$$

It follows from formula (59.8) that

$$\frac{\mu_0}{\mu_B H} = [R_{3/2}(x)]^{2/3}, \tag{59.10}$$

and, using expression (59.7), we find

$$\frac{\mu(H, 0)}{\mu_0} = x\,[R_{3/2}(x)]^{-2/3}. \tag{59.11}$$

Finally, substituting formula (59.10) in Eq. (59.9), we obtain

$$\frac{\chi(H, 0)}{\chi_0} = [R_{5/2}(x) - xR_{3/2}(x)]\,\{R_{3/2}(x)\}^{-1/3}, \tag{59.12}$$

where

$$\chi_0 = \frac{N}{V}\frac{\mu_B^2}{\mu_0}.$$

Formulae (59.10) through (59.12) present in parametric form the dependence of $\mu(H, 0)/\mu_0$ and $\chi(H, 0)/\chi_0$ on $\frac{\mu_0}{\mu_B H}$ (Fig. 78), i.e. on the intensity of the magnetic field at absolute zero. It can be seen from these formulae that the behaviour of the quantities $\mu(H, 0)/\mu_0$

and $\chi(H, 0)/\chi_0$ is determined by the properties of the functions $R_{5/2}(x)$ and $R_{3/2}(x)$. Since the derivative of the function $R_{3/2}(x)$, equal to $\frac{3}{2} R_{1/2}(x)$, has (infinite) discontinuities at points $x = 2l$, characteristic peaks are observed in Fig. 78. It is seen from the figure that both $\mu(H, 0)$ and $\chi(H, 0)$ are oscillating functions of $\frac{\mu_0}{\mu_B H}$. With decreasing field intensity H the oscillations of the chemical potential $\mu(H, 0)$ attenuate rapidly and the chemical potential μ reaches its practical limit μ_0 at $\frac{\mu_0}{\mu_B H} \sim 10$.

The susceptibility $\chi(H, 0)$ undergoes greater oscillations. As can be seen from Fig. 78, the susceptibility becomes negative at some

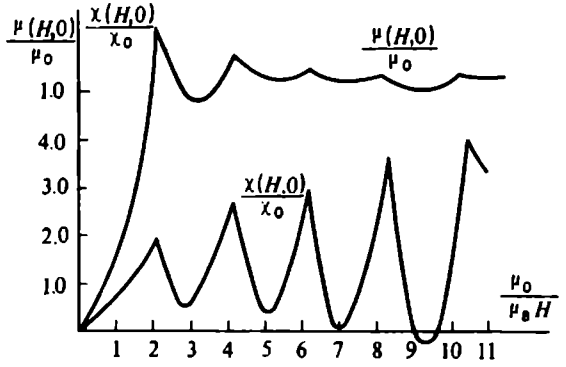


FIG. 78

values of H, which is indicative of the predominance of the diamagnetic effect over the paramagnetic one. The critical fields $H = H_l$, at which the derivatives of the functions $\mu(H, 0)$, $\chi(H, 0)$ have discontinuities, are determined from the condition

$$x_l = \frac{\mu(H_l, 0)}{\mu_B H_l} = 2l.$$

It is now possible to relate the period of oscillation for the susceptibility ΔH_l and the field intensity H_l at which this oscillation is observed. Write down the formulae:

$$\frac{\mu(H_l, 0)}{\mu_B H_l} = 2l, \quad \frac{\mu(H_l + \Delta H_l, 0)}{\mu_B (H_l + \Delta H_l)} = 2(l-1).$$

Taking the difference of the two expressions and allowing for the relatively weak dependence of $\mu(H, 0)$ on H (especially at large l), we obtain

$$\frac{\mu(H_l, 0)}{H_l} - \frac{\mu(H_l + \Delta H_l, 0)}{H_l + \Delta H_l} = 2\mu_B,$$

or

$$\frac{\left(\mu_0+\frac{\partial\mu}{\partial H}H_l\right)(H_l+\Delta H_l)-\left[\mu_0+\frac{\partial\mu}{\partial H}(H_l+\Delta H_l)\right]H_l}{H_l(H_l+\Delta H_l)}=2\mu_B,$$

whence, finally, we find the rule

$$\frac{2H_l(H_l+\Delta H_l)}{\Delta H_l}=\frac{\mu_0}{\mu_B}=\text{const},$$

which agrees well with experimental data.

Let us consider two extreme cases.

Strong fields: $x=\frac{\mu_0}{\mu_B H}<2$.

As can be seen from Fig. 78, within the range $0<x<2$, corresponding to the interval $0<\frac{\mu_0}{\mu_B H}<[R_{3/2}(2)]^{2/3}=4.5^{1/3}$, the oscillations of the chemical potential and susceptibility, characteristic of weak fields, vanish and $\mu(H, 0)$ and $\chi(H, 0)$ decrease monotonically with increasing field intensity. This region is of no practical interest and is hardly attainable.

At $0<x<2$ formula (59.7) gives

$$R_{5/2}(x)=\frac{5}{2}x^{3/2},\quad R_{3/2}(x)=\frac{3}{2}x^{1/2},$$

and, making use of formulae (59.10) through 59.12), we find

$$\frac{\mu(H, 0)}{\mu_0}=\left(\frac{2}{3}\right)^{2/3}x^{2/3},\quad \frac{\chi(H, 0)}{\chi_0}=\frac{2}{3}x^{4/3},\quad \frac{\mu_0}{\mu_B H}=\left(\frac{3}{2}\right)^{2/3}x^{1/3}.$$

Eliminating from the above formulae the parameter x, we obtain

$$\frac{\mu(H, 0)}{\mu_0}=\frac{4}{9}\left(\frac{\mu_0}{\mu_B H}\right)^2,\quad \frac{\chi(H, 0)}{\chi_0}=\frac{8}{27}\left(\frac{\mu_0}{\mu_B H}\right)^4.$$

Weak fields: $x\gg 1$. Let us derive the asymptotic expressions for the functions $R_a(x)$ at large values of the argument x. According to formula (59.7), we have

$$a^{-1}R_a(2l)=(2l)^{a-1}+2^a[1^{a-1}+2^{a-1}+\ldots+(l-1)^{a-1}]$$

$$=2^a\sum_{n=1}^{l}n^{a-1}-(2l)^{a-1}.$$

The above expression can be estimated by means of the Euler sum formula

$$\sum_{n=0}^{l}f(n)=\int_0^l f(x)\,dx+\frac{1}{2}[f(0)+f(l)]+\ldots.$$

According to this formula, we have

$$\sum_{n=0}^{l} n^{a-1} = \frac{l^a}{a}\left(1 + \frac{a}{2l} + \ldots\right),$$

whence for large values of x we obtain

$$R_a(x) = x^a\left[1 + \frac{a(a-1)}{3x^2} + \ldots\right].$$

Formulae (59.11) and (59.12) are used to calculate

$$\frac{\mu(H, 0)}{\mu_0} \approx 1 - \frac{1}{6x^2}, \quad \frac{\chi(H, 0)}{\chi_0} \approx 1 - \frac{1}{20x^2}, \quad x = \frac{\mu_0}{\mu_B H}.$$

Eliminating x, we obtain

$$\frac{\mu(H, 0)}{\mu_0} \approx 1 - \frac{1}{6}\left(\frac{\mu_B H}{\mu_0}\right)^2, \quad \frac{\chi(H, 0)}{\chi_0} \approx 1 - \frac{1}{20}\left(\frac{\mu_B H}{\mu_0}\right)^2.$$

The nature of the dependence of $\chi(H, T)$ and $\mu(H, T)$ on the magnetic field in the low temperature region $T \ll \mu_B H$ is the same as at absolute zero, only at values of the parameter $x = 2l$ the peaks vanish with rising temperature and are replaced by smooth transitions with a width of the order of $\frac{T}{\mu_B H}$. The width of these transition regions increases with rising temperature, the curves flatten out and the oscillating nature of the curves, which is characteristic of strong fields, becomes less pronounced.

Let us consider the extreme case of high temperatures $T \gg \mu_0$. In this case, as will become evident later, μ/T is a large negative number and $e^{(\mu-\varepsilon)/T} \ll 1$. It is, therefore, convenient to calculate $\Omega(\mu, H, T)$ directly by formula (59.2) without recourse to the general integral formula. Substituting $\varepsilon(q)$ from formula (59.1) and passing to integration, we obtain

$$-\Omega(\mu, H, T) = T\sum_{(q)} e^{\beta[\mu-\varepsilon(q)]}$$

$$= e^{\mu/T}\frac{V}{h^3}\frac{eHT}{c}\int_{-\infty}^{\infty}(e^{\beta\mu_B H} + e^{-\beta\mu_B H})\sum_{n=0}^{\infty} e^{-\beta\mu_B H(2n+1)}e^{-\beta p_z^2/2m}\,dp_z.$$

Performing integration

$$\int_{-\infty}^{\infty} e^{-\beta p_z^2/2m}\,dp_z = \left(\frac{2\pi m}{\beta}\right)^{1/2} = (2\pi m T)^{1/2}$$

and summation

$$\sum_{n=0}^{\infty} e^{-\beta\mu_B H(2n+1)} = (e^{\mu_B H/T} - e^{-\mu_B H/T})^{-1},$$

we obtain

$$-\Omega(\mu, H, T) = \frac{V}{4}\left(\frac{8\pi m}{h^2}\right)^{3/2} T^{5/2} e^{\mu/T} \frac{\mu_B H}{T} \coth \frac{\mu_B H}{T}.$$

The above formula yields

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, H} = \frac{V}{4}\left(\frac{8\pi m T}{h^2}\right)^{3/2} e^{\mu/T} \frac{\mu_B H}{T} \coth \frac{\mu_B H}{T}$$

and, taking the logarithm, we find the chemical potential

$$\mu = -T \ln \left\{\frac{V}{4N}\left(\frac{8\pi m T}{h^2}\right)^{3/2} \frac{\mu_B H}{T} \coth \frac{\mu_B H}{T}\right\}. \qquad (59.13)$$

Formula (59.13) indicates that at $T \gg \mu_0$ and any H, $\mu(H, T)/T$ is in fact a large negative number. By analogy, we have

$$M(H, T) = -\frac{1}{V}\left(\frac{\partial \Omega}{\partial H}\right)_{\mu, T}$$
$$= \frac{T^{5/2}}{4H}\left(\frac{8\pi m}{h^2}\right)^{3/2} e^{\mu/T}\left[\frac{\mu_B H}{T} \coth \frac{\mu_B H}{T} - \left(\frac{\mu_B H}{T}\right)^2 \sinh^{-2} \frac{\mu_B H}{T}\right].$$

Eliminating μ and introducing the maximum magnetization per unit volume, $M_0 = N\mu_B/V$, we obtain

$$\frac{M(H, T)}{M_0} = \frac{T}{\mu_B H}\left[1 - \frac{2\mu_B H/T}{\sinh(2\mu_B H/T)}\right]. \qquad (59.14)$$

Formula (59.14) is derived for high temperatures with the account taken of both the diamagnetic and the paramagnetic effects. While expression (51.11) leads to saturation in strong fields (curve *1* in Fig. 79), $M \to M_0$ as $H \to \infty$, expression (59.14) points to monotonically decreasing magnetization M in strong fields, $M \propto H^{-1}$ (curve *2* in Fig. 79). All traces of oscillations in the quantities $\mu(H, T)/\mu_0$ and $\chi(H, T)/\chi_0$ naturally disappear at high temperatures.

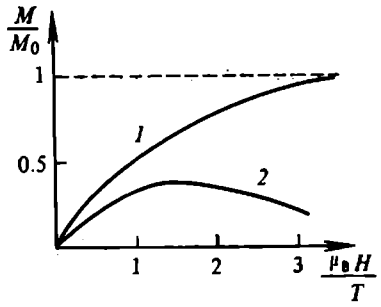


FIG. 79

In concluding this section, let us consider the simple and physically vivid interpretation of the de Haas-Van Alphen effect, examining a more general anisotropic model of a metal and making sure that experimental study of the oscillation of magnetic susceptibility provides important data on the form of an anisotropic Fermi surface (for greater detail see [13]).

In a quasi-classical approximation, suitable for most metals with any attainable field, the energy levels of finite electron motion in a

magnetic field are determined by the Bohr-Sommerfeld quantization rule

$$\oint \mathbf{P}_\perp \, d\mathbf{r} = nh, \tag{59.15}$$

where $\mathbf{P}_\perp$ is the component of a generalized momentum in the XOY plane perpendicular to $\mathbf{H}$. Let us calculate the integral on the right-hand side, using normalization of the vector potential

$$A_x = -Hy, \quad A_y = A_z = 0,$$

whence

$$P_x = p_x - \frac{eH}{c} y, \quad P_y = p_y.$$

Since the coordinate x is a cyclic one, $P_x = \text{const}$ and $dy = \frac{c}{eH} dp_x$.

From this we find $\mathbf{P}_\perp \, d\mathbf{r} = P_x dx + P_y dy = P_x dx + \frac{c}{eH} p_y \, dp_x$. The contour integral of the first term is equal to zero since $P_x = \text{const}$, and we obtain

$$\oint \mathbf{P}_\perp \, d\mathbf{r} = \frac{c}{eH} \oint p_y \, dp_x$$

$$= \frac{c}{eH} S(\varepsilon, p_z),$$

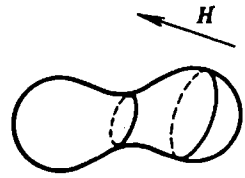


FIG. 80

where $S(\varepsilon, p_z)$ is the area of the surface $\varepsilon = \text{const}$ intersected by the plane perpendicular to the direction of the magnetic field. The condition of energy quantization (59.15) then acquires the following form:

$$\frac{c}{ehH} S(\varepsilon, p_z) = n.$$

Depending on H^{-1}, the oscillation period for susceptibility is evidently determined by the condition $\Delta n = 1$ (the filling of a new orbital terminates). From this we find

$$\Delta(H^{-1}) = \frac{eh}{cS(\varepsilon, p_z)} \tag{59.16}$$

The oscillating nature of the dependence of susceptibility on H is blurred by the functional dependence of S on p_z. It is clear that the main contribution to the oscillation effects is made by the values of p_z at which $S(\varepsilon, p_z)$ changes slowly with p_z, or, in other words, the extreme sections of the constant-energy surface (Fig. 80). In addition, it is clear that at low temperatures $T < \mu_B H \ll \mu_0$ it is precisely the Fermi surface $\varepsilon = \mu_0$ which is of importance to the problem. For this reason formula (59.16) allows us, by changing the

direction of the magnetic field and measuring the oscillation periods, to obtain data on the extreme sections of the Fermi surface and, thereby, on its form. However, the intricate nature of the Fermi surface (the great number of extreme cross sections) and a number of subordinate effects, such as the interaction of electrons with phonons and also with impurity atoms, considerably complicate the problem of restoring the Fermi surface based on experimental data (for greater detail see [13]).

Problem

Show that for an isotropic model—a spherical Fermi surface—formula (59.16) is qualitatively in agreement with formula (59.13).

CHAPTER VI

SYSTEMS OF INTERACTING PARTICLES. THE GIBBS METHOD

60. Γ-space. Liouville's Theorem

Up till now we have limited ourselves to the consideration of problems that could be solved by the method of boxes and cells, i.e. of problems of the thermodynamic properties of ideal gases.

The following sections will be devoted to a much more general method of solving problems in statistical physics, the *Gibbs method*, which allows us to investigate the behaviour of arbitrary macroscopic systems whose component particles interact with any degree of strength. It is clear that the results that can be obtained from applying Gibbs's method include as a particular case all the results that have been obtained by means of the box-and-cell method.

First, we have to introduce the concept of the phase Γ-space, which is a direct generalization of the concept of the μ-space. If interaction exists between particles, a change in the coordinates and momenta of one particle entails a change in the coordinates and momenta of other particles. This means that the μ-spaces of individual particles are no longer independent of each other and a solution based only on the concept of the μ-space is inadequate.

Let us mean by the Γ-space a $2Nf$-dimensional continuum whose coordinates are Nf generalized coordinates and Nf generalized momenta of all particles, where N is the number of system's particles and f is the number of degrees of freedom of each particle. A point in the Γ-space represents the state of an entire system, and not of one molecule, as was the case with the μ-space. The state of the system evolutionizes in the course of time and the representative point traverses a phase trajectory which lies on a constant-energy hypersurface in the case of a closed system:

$$E = \sum_i \mathcal{K}_i + \sum_i \mathcal{U}(q_i) + \mathcal{W}(q_1, q_2, \ldots), \tag{60.1}$$

where $\mathcal{K}_i$ = kinetic energy of ith particle;

$\mathcal{U}(q_i)$ = potential energy of the ith particle in an external field;

$\mathcal{W}\{q_i\}$ = potential energy of particle interaction.

By analogy with the μ-space, the product of the differentials of all coordinates and momenta will be referred to as the element of volume in the phase Γ-space:

$$d\Gamma = \prod_i dq_i\, dp_i. \tag{60.2}$$

Just as in the case of an ideal gas, making a quasi-classical description with the aid of coordinates and momenta, each quantum state will be assigned a phase volume h^{Nf}, so that the expression

$$d\Omega = \frac{d\Gamma}{h^{Nf}} \tag{60.3}$$

represents the number of quantum states taken over for the intervals q_i, $q_i + dq_i$ and p_i, $p_i + dp_i$ of the generalized coordinates and momenta.

The Gibbs method is based on the following. Let us consider the selected system, placing it into a surrounding medium (a thermostat). The microstate of the system will change in the course of time due to interaction with the surroundings, following a rather complicated law. It is practically impossible and even not necessary to predict in advance the progress of these changes due to the enormous number of dergees of freedom, since of interest to us is the macroscopic state of the system, and not the state of each component particle. We can only assert that a representative point can move in the phase space along an extremely tangled trajectory, passing repeatedly through any rather small volume of the phase space. This trajectory lies no more on the constant-energy surface, since due to the interaction with the surroundings, the system's energy also changes slowly. This permits us the introduction of the probability of finding a representative point in any element of the phase volume, proportional to $d\Gamma$:

$$dW(p, q) = \rho(p, q)\, d\Gamma, \tag{60.4}$$

where $\rho(p, q)$ is the system's probability density or distribution function (the symbols p, q will be used to denote the set of the generalized coordinates and momenta). The function $\rho(p, q)$ must evidently satisfy the normalization condition

$$\int \rho(p, q)\, d\Gamma = 1. \tag{60.5}$$

The mean value of any function of coordinates and momenta can be calculated by the formula

$$\bar{L} = \int L(p, q)\, \rho(p, q)\, d\Gamma. \tag{60.6}$$

If we follow a representative point in the phase space and mark its position on the phase trajectory in small time intervals, then the totality of these instantaneous positions of the representative point in a sufficiently long time will fill the Γ-space with a density proportional to $\rho(p, q)$. The method suggested by Gibbs consists in that instead of tracing the motion of one representative point in the course of time, we visualize a set of representative points distributed in the

Γ-space with a density $\rho(p, q)$. This means that we can think of a set of copies of the same physical system, differing from each other only in the values of p_i and q_i at a certain moment of time, that can be chosen as reference, $t = 0$.

If we examine, for instance, the behaviour of a gas confined within a vessel, we must visualize an enormous number of gas-holding vessels; if we consider a crystal, we must think of a great number of similar pieces of the crystal, etc. The copies of the system may have different volumes and be composed of different numbers of particles, but be placed in the same surroundings. Such collectives of (imaginary) copies of a system are called *statistical ensembles*, and below (see Secs. 61, 62) we shall consider various particular cases of such ensembles, depending on which parameters are fixed in an ensemble (energy, temperature, volume, number of particles, etc.). Due to the different initial conditions and interaction with the surroundings, the state of each copy changes with time in a different way, meaning that each representative point, describing the state of one of the ensemble copies, moves along its phase trajectory. The set of these points forms in the Γ-space a gas, or rather a liquid with density $\rho(p, q, t)$.

Let us derive the equation describing the function $\rho(p, q, t)$. Since the representative points neither appear, nor vanish—the number of copies in an ensemble is constant, the decrease in the number of representative points in fixed volume Γ of the phase space per unit time, equal to $-\int_\Gamma \rho(p, q, t)\, d\Gamma$, must coincide with the flux of the number of representative points through the boundary of volume Γ. Hence,

$$-\frac{d}{dt}\int_\Gamma \rho(p, q, t)\, d\Gamma = -\int_\Gamma \frac{\partial \rho}{\partial t}\, d\Gamma = \oint \rho \mathbf{u}\, d\sigma, \qquad (60.7)$$

where $\mathbf{u}$ = vector of the $2fN$-dimensional velocity of the representative points ($\mathbf{u}$ has the projections $\dot{q}_k$ and $\dot{p}_k$, $k = 1, 2, \ldots, fN$);

$d\sigma$ = directional surface element confining the volume Γ.

Making use of Gauss' theorem, we transform the surface integral on the right-hand side of Eq. (60.7) into a volume integral, obtaining

$$\int_\Gamma \left[\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{u})\right] d\Gamma = 0$$

or, due to the arbitrariness of Γ,

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{u}) = 0 \qquad (60.8)$$

(∇ is a $2fN$-dimensional gradient with projections $\frac{\partial}{\partial q_k}$, $\frac{\partial}{\partial p_k}$). Equation (60.8) is an ordinary *continuity equation*, merely reflecting the fact that the number of representative points is constant.

Vector **u** contains information on system properties. The system will be assumed to be closed or quasi-closed and the effect of the surroundings on system particles will be ignored. This effect takes place only in the thin surface layer with a thickness of the order of the range of molecular forces and is negligibly small in the course of sufficiently small time intervals. Limiting ourselves to the consideration of classical systems, the Hamiltonian will be assumed to depend only on the coordinates and momenta of system particles, $\mathcal{H} = \mathcal{H}(q, p)$. Then, the equation of motion in the Hamiltonian form

$$\dot{q}_k = \frac{\partial \mathcal{H}}{\partial p_k}, \quad \dot{p}_k = -\frac{\partial \mathcal{H}}{\partial q_k} \tag{60.9}$$

permits an important transformation of the second term in formula (60.8):

$$\nabla(\rho \mathbf{u}) = \sum_{k=1}^{fN} \left[\frac{\partial}{\partial q_k}(\rho \dot{q}_k) + \frac{\partial}{\partial p_k}(\rho \dot{p}_k) \right]$$

$$= \rho \sum_{k=1}^{fN} \left[\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right] + \sum_{k=1}^{fN} \left[\frac{\partial \rho}{\partial p_k} \dot{q}_k + \frac{\partial \rho}{\partial p_k} \dot{p}_k \right].$$

The first term on the right-hand side equals zero, since, according to formula (60.9),

$$\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} + \frac{\partial^2 \mathcal{H}}{\partial q_k \partial p_k} - \frac{\partial^2 \mathcal{H}}{\partial p_k \partial q_k} = 0,$$

and the second term is a scalar product $\mathbf{u}\nabla\rho$. Therefore we obtain an equation, describing the behaviour of an ensemble of classical quasi-closed systems, if interaction with surroundings is ignored,

$$\frac{\partial \rho}{\partial t} + \mathbf{u}\nabla\rho = 0, \tag{60.10}$$

referred to as *Liouville's equation.*

It should be noted that the sum

$$\frac{\partial \rho}{\partial t} + \mathbf{u}\nabla\rho = \frac{\partial \rho}{\partial t} + \sum_i \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right] = \frac{d\rho}{dt}$$

is the total derivative of $\rho(p, q, t)$ with respect to time. With the account of the equations of motions (60.9), the sum can also be presented

in the following form:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, \mathcal{H}], \text{ where } [A, B] = \sum_l \frac{\partial A}{\partial q_l}\frac{\partial B}{\partial p_l} - \frac{\partial A}{\partial p_l}\frac{\partial B}{\partial q_l}$$

are the classical Poisson brackets. In this connection formula (60.10) can be presented in two more forms:

$$\frac{d\rho}{dt} = 0, \tag{60.11}$$

$$\frac{\partial \rho}{\partial t} + [\rho, \mathcal{H}] = 0. \tag{60.12}$$

It follows from (60.11) that the distribution function $\rho\ (p, q, t)$ remains constant along the dynamic trajectories in the Γ-space. This assertion is referred to as Liouville's theorem. Here, by the dynamic trajectories are meant the lines whose parametric equations $q_k = q_k\ (t)$, $p_k = p_k\ (t)$ are derived from the equations of motion (60.9).

Liouville's equation plays an important role in studying the laws governing the evolution of the state of macroscopic systems with time, and it will be studied in greater detail in Ch. IX, devoted to kinetics. In statistical physics, we shall limit ourselves to the considering of equilibrium and, consequently, stationary states, so that the distribution function is constant, $\frac{\partial \rho}{\partial t} = 0$, at each point of the Γ-space. Liouville's equation then reduces to

$$\mathbf{u}\ \nabla \rho = 0, \tag{60.13}$$

or

$$[\rho, \mathcal{H}] = 0. \tag{60.14}$$

It can be seen from Eq. (60.13) that in a stationary state the gradient of the distribution function is normal to the dynamic trajectory, so that the distribution function does not change along the trajectory.

Thus, the distribution function $\rho\ (p, q)$ is an integral of motion. Furthermore, it is clear that $\rho\ (p, q)$ is a multiplicative quantity and its logarithm is an additive integral of motion. Indeed, subdividing mentally the system under consideration into two macroscopic subsystems I and II with linear dimensions of the order of l, we can assume them to be statistically independent. Due to the small range of molecular forces, only those particles interact that are arranged in the thin layer close to the subsystem interface, but the number of such particles and the interaction energy are proportional to l^2, while the total number of particles and the internal energy are proportional to l^3, therefore for macroscopic subsystems the interaction energy is small compared to the internal energy.

Thus, the subsystems are quasi-closed, and the instantaneous state of one subsystem does not affect the state of the other. It should

be noted, however, that over prolonged time intervals the interaction of the two subsystems, just as the interaction of the system with the surroundings, manifests itself if only in that the energy of each subsystem and of the system as a whole changes slowly and the representative point passes from one constant-energy hypersurface to another. Due to the statistical independence of the subsystems and according to the probability multiplication theorem, we can describe the probability of finding the entire system in an element $d\Gamma$ of the phase space by the expression

$$dW(p, q) = \rho(p, q)\, d\Gamma = \rho_1\, d\Gamma_1\, \rho_2\, d\Gamma_2.$$

Since $d\Gamma = d\Gamma_1\, d\Gamma_2$, then

$$\rho = \rho_1 \rho_2, \quad \ln \rho = \ln \rho_1 + \ln \rho_2. \tag{60.15}$$

For most physical systems there exist only seven independent additive integrals of motion: energy, three projections of one system's momentum **P** and three projections of the system's angular momentum **M**. The probability density $\rho(p, q)$ is a function of them. Below, bodies will be treated in a frame of reference in which the bodies as a whole are not in translational motion, i.e. $\mathbf{P} = 0$, and do not rotate, i.e. $\mathbf{M} = 0$. In this case we assume that the probability density $\rho(p, q)$ is a function only of energy:

$$\rho(p, q) = \rho(E). \tag{60.16}$$

61. Microcanonical and Canonical Distributions

The simplest statistical distribution, obeying formula (60.16), is obtained, assuming the system to be *closed*, or isolated. The probability density $\rho(p, q)$ then differs from zero only on the constant-energy hypersurface. Inasmuch as the normalization condition (60.5) must be satisfied and the number of dimensions of the constant-energy hypersurface $E(p, q) = \widetilde{E}$ is less by unity than the number of dimensions of the Γ-space, it is clear that $\rho(p, q)$ must become infinity at $E(p, q) = \widetilde{E}$. This can be described conveniently by means of Dirac's δ-function

$$\rho(p, q) = \Lambda \delta[E(p, q) - \widetilde{E}], \tag{61.1}$$

where Λ is a constant defined by the normalization condition. Formula (61.1) expresses the *Gibbs microcanonical distribution.*

It is often useful to indicate implicitly that not only the energy E, but also the number of particles N and the system's volume $\widetilde{V}$ are fixed. Then, the microcanonical distribution will be written down in the form

$$\rho(p, q) = \Lambda \delta[E(p, q) - \widetilde{E}]\, \delta(V - \widetilde{V}) \delta_{N, \widetilde{N}}. \tag{61.2}$$

Let us derive now the statistical distribution for an *open* system interacting with the surroundings. Such a distribution will be derived in this section for an arbitrary macroscopic system, assuming, firstly, the system's surroundings to be an ideal gas and a thermostat and, secondly, the system to be placed in a vessel with heat-transferring walls, fixed and impermeable to system's particles, so that there is energy exchange between the thermostat and the system; the number of particles in the system and system volume are assumed to be fixed, $N = \text{const}$, $V = \text{const}$. (Both the first and second assumption will be renounced in the next section.)

Denote by $E(p, q)$ the system's energy, by $\varepsilon(P) = \sum_{i=1}^{3N} \frac{P_i^2}{2m}$ the energy of the thermostat and by $\widetilde{E}$ the total energy (q, p are the generalized coordinates and momenta of system's particles, Q and P denote the coordinates and momenta of thermostat's particles), and by N the number of particles in the thermostat.

The system under consideration + the thermostat are assumed to be a closed combined system for which the following microcanonical distribution is true:

$$\rho(p, q, P, Q) = A\delta(E + \varepsilon - \widetilde{E}). \tag{61.3}$$

To find the system's distribution function which determines the probability that system's coordinates and momenta lie in the elementary phase volume $d\Gamma$, expression (61.3) must be integrated over the coordinates and momenta of thermostat's particles, Q and P. Evaluate the integral

$$\int\int d^{3N}Q\, d^{3N}P\, \delta\left(\sum_{i=1}^{3N} \frac{P_i^2}{2m} + E - \widetilde{E}\right). \tag{61.4}$$

Integration over the coordinates Q yields V^N due to the fact that the integrand is independent of Q.

To carry out the integration in the momentum space of thermostat's particles, let us pass to spherical coordinates. Denote the volume of a $3N$-dimensional sphere by $V_{3N} = C_{3N}R^{3N}$, where C_{3N} is a dimensionless constant [see Mathematical Appendix, formula (XIII.5)] and R is the sphere radius in the $3N$-dimensional space, determined by

$$R = \left[\sum_{i=1}^{3N} P_i^2\right]^{1/2} = (2m\varepsilon)^{1/2}, \quad dR = \left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon.$$

Then, the element of volume is equal to

$$dV_{3N} = 3NC_{3N}R^{3N-1}\, dR = \frac{3}{2} NC_{3N}(2m)^{3N/2}\, \varepsilon^{3N/2-1}\, d\varepsilon$$

and, consequently,

$$\int\int d^{3N}Q\, d^{3N}P\, \delta\left(\sum_{i=1}^{3N}\frac{P_i^2}{2m}+E-\widetilde{E}\right)$$

$$=\frac{3N}{2}C_{3N}V^N(2m)^{3N/2}\int \varepsilon^{3N/2-1}\delta(\varepsilon+E-\widetilde{E})\,d\varepsilon$$

$$=D(N)\left(1-\frac{E}{\widetilde{E}}\right)^{3N/2-1},$$

where $D(N)$ denotes the totality of all multipliers independent of the system's energy.

Let us pass now to the limit $N\to\infty$, assuming the number of particles to remain large but finite. Since the thermostat is an ideal gas, then $\frac{\widetilde{E}}{N}\approx\frac{\varepsilon}{N}=\frac{3}{2}T$ and

$$\left(1-\frac{E}{\widetilde{E}}\right)^{3N/2-1}\approx\left(1-\frac{E}{3NT/2}\right)^{3N/2}\to e^{-E/T}. \tag{61.5}$$

Introducing the notation $\Lambda D(\infty)=1/Z$, we find from formulae (61.3) and (61.5) that

$$\rho(p,q)=\frac{e^{-E(p,q)/T}}{Z}. \tag{61.6}$$

The distribution obtained is known as the *Gibbs canonical distribution.* The quantity Z is determined by the normalization condition $\int\rho(p,q)\,d\Gamma=1$ and, similar to the Maxwell-Boltzmann distribution, is referred to as the integral of states* (see Sec. 37)

$$Z=\int e^{-E(p,q)/T}\,d\Gamma. \tag{61.7}$$

Since, according to formula (61.6), the probability density $\rho(p,q)$ depends only on energy, the probability that system's energy lies within $(E, E+dE)$ is equal to

$$dW(E)=\rho(E)\,dE=e^{-E/T}\,d\Gamma(E)/Z, \tag{61.8}$$

where $d\Gamma(E)=\frac{d\Gamma}{dE}\,dE$ is the volume of the phase space between the hypersurfaces $E(p,q)=E$ and $E(p,q)=E+dE$.

In the derivation presented above, the thermostat was assumed to be an ideal Maxwell-Boltzmann gas. It is clear from the physical viewpoint that the result (61.6) must not depend on the selection of thermostat and must remain valid also in the case when a Bose gas, a Fermi gas, a real gas, etc., is chosen as a thermostat.

* It should be emphasized that in contrast to Boltzmann's integral of states, the integral in (61.7) is taken over the phase space of the entire system.

Integration over the Γ-space of the thermostat in formula (61.4) can readily be performed only if the thermostat is a Maxwell-Boltzmann gas in which the coordinates and momenta of the particles are not correlated. In all other cases, including those involving Bose- and Fermi gases, such correlations exist. In the case of fermions there exist, by virtue of the Pauli exclusion principle, repulsive forces between particles closely arranged to each other in the Γ-space, while for bosons there is a tendency toward particle accumulation in one state. This means that different regions of the Γ-space become non-equivalent, and the integration in formula (61.4) must be performed with some weight factor accounting for the correlations, and this would hamper greatly the solution of the problem.

Let us point out now another important property of the canonical distribution presented by formula (61.8). For macroscopic systems the function $\frac{d\Gamma}{dE}$ increases rapidly with E, while the exponential $e^{-E/T}$ decreases rapidly with rising E. For this reason the product of the two functions has a sharp maximum at a certain value of energy $E = E_{\text{prob}}$, meaning that in a canonical ensemble energy fluctuations are very small and $\frac{dW(E)}{dE} = \rho(E)$ behaves practically as $\delta(E - E_{\text{prob}})$. Therefore the Gibbs canonical distribution is actually equivalent to the microcanonical distribution. In particular, the most probable energy, E_{prob}, coincides with a great accuracy with the mean energy $\bar{E} = U$.

Let us illustrate the foregoing by considering an ideal gas, for which, as was shown above,

$$\frac{d\Gamma}{dE} \propto E^{3N/2-1},$$

and we have

$$\rho(E) = \text{const} \cdot E^{3N/2-1} e^{-E/T}. \tag{61.9}$$

Let us find the maximum of $\rho(E)$. Differentiating Eq. (61.9) and equating the derivative to zero, we find

$$E_{\text{prob}} = \left(\frac{3N}{2} - 1\right) T$$

and, comparing with $\bar{E} = \frac{3N}{2} T$, we see that

$$\frac{\bar{E} - E_{\text{prob}}}{\bar{E}} = \frac{2}{3N},$$

i.e. for macroscopic systems the difference between $\bar{E}$ and E_{prob} is negligibly small.

Let us find the form of the distribution function $\rho(E)$ in the neighbourhood of E_{prob} where it differs markedly from zero. We rewrite

expression (61.9) to read

$$\rho(E) = e^{\varphi(E)},$$

where

$$\varphi(E) = -\frac{E}{T} + \left(\frac{3N}{2} - 1\right) \ln E + \text{const},$$

and expand the function $\varphi(E)$ into a series in $(E - E_{\text{prob}})$:

$$\varphi'(E_{\text{prob}}) = 0, \quad \varphi''(E_{\text{prob}}) = -\frac{3N/2-1}{E^2_{\text{prob}}} \approx -\frac{3N}{2E^2_{\text{prob}}},$$

whence

$$\rho(E) = \text{const} \cdot \exp\left[-\frac{3N}{4}\frac{(E-E_{\text{prob}})^2}{E^2_{\text{prob}}}\right].$$

Thus, close to the maximum the canonical distribution acquires the form of the Gaussian distribution. For a numerical estimation of the maximum sharpness we assume $N \sim 10^{19}$ and $(E - E_{\text{prob}})/E_{\text{prob}} \sim 10^{-5}$ and obtain $\rho(E)/\rho(E_{\text{prob}}) \sim 10^{-10^9}$. Hence the maximum of a canonical distribution is so sharp that it cannot be presented graphically on any practically feasible scale. The distribution is practically delta-shaped and is equivalent thermodynamically to the microcanonical distribution.

62. T-V-μ and T-P-N Distributions

In the preceding section we considered the statistical distribution for systems whose energy can fluctuate, but the number of particles in a system and its volume are fixed. This signifies that the system, placed into a thermostat with T = const, is contained in a vessel whose walls possess a high thermal conductivity, are stationary (V = const) and impermeable to particles of the system and the surroundings (N = const). Below systems of this kind will be referred to as T-V-N systems.

In practice, however, we are also concerned with systems with a fluctuating number of particles (for instance, a liquid or a crystal in equilibrium with vapour, a phonon- or photon gas). Let us visualize a system confined in a vessel with heat-conducting stationary walls permeable for particles. The system is then in equilibrium with the thermostat (T = const) with which it can exchange not only energy but also particles ($N \neq$ const). Such equilibrium requires that the chemical potentials of the system and of the surroundings should be the same, i.e. the condition imposed is μ = const. Systems characterized by T = const, V = const, μ = const will be referred to as T-V-μ systems, and the corresponding distribution, to be derived below, as the *Gibbs grand canonical distribution.*

Finally, a system can be visualized in which, in addition to energy, the volume fluctuates, and the number of particles remains constant—the system is confined within a vessel with heat-conducting walls impermeable for particles, closed with a frictionless piston. It is also clear that in this case the pressure in the system and surroundings must be the same, and the condition imposed is $P = \text{const}$. Systems with $T = \text{const}$, $P = \text{const}$ and $N = \text{const}$ will be called *T-P-N* systems.

Let us turn to the derivation of the Gibbs grand canonical distribution, assuming, as in the preceding section, the thermostat to be an ideal gas with a number of particles N great compared with the number of system's particles. The thermostat is separated from the system by a stationary partition permeable for particles. For a combined system the microcanonical distribution is valid:

$$\rho(p, q, n, P, Q, N) = \Lambda\delta\left[\sum_{i=1}^{N}\frac{P_i^2}{2m} + E(p, q) - \tilde{E}\right], \qquad (62.1)$$

$$n + N = \tilde{N} = \text{const}.$$

Of interest to us is the probability density $\rho(p, q, n)$ for a system consisting of n particles. To find the probability density, we must integrate Eq. (62.1) over the coordinates and momenta of thermostat's particles and multiply the expression obtained by the number of ways in which $\tilde{N}$ particles can be distributed between the system and the thermostat, $\frac{\tilde{N}!}{n!N!}$. For this factor there is the approximate expression $\frac{\tilde{N}!}{n!N!} = \frac{1}{n!}(N+1)(N+2) \ \ldots \ (N+n) \approx \frac{N^n}{n!}$.

Integration over Q_i and P_i is performed in exactly the same way as in the preceding section, resulting in

$$\rho(p, q, n) = \frac{\tilde{N}!\,\Lambda}{n!\,N!}\int\int d^3Q_i\, d^3P_i\,\delta\left(\sum_i \frac{P_i^2}{2m} + E - \tilde{E}\right)$$

$$= \frac{\Lambda N^n}{n!}V^N\frac{3}{2}NC_{3N}\frac{(2m\tilde{E})^{3N/2}}{\tilde{E}}\left(1 - \frac{E}{\tilde{E}}\right)^{3N/2-1}. \qquad (62.2)$$

Upon the substitution $\tilde{E} \approx \frac{3}{2}NT$ and, passing to the limit $N \to \infty$, the last factor in formula (62.2) gives the Gibbs factor $e^{-E/T}$. In the remaining factors N is replaced by $\tilde{N} - n$ and, using formula (XIII.10) of Mathematical Appendix for C_{3N}, all factors independent of n are gathered into one common factor $Q(\tilde{N}, \tilde{E}, V)$. According to formula (XIII.10), at $\tilde{N} \gg n$, with an accuracy to factors

independent of n we have

$$NC_{3N} = N\left(\frac{2\pi e}{3N}\right)^{3N/2}$$

$$\sim \left(\frac{3\widetilde{N}}{2\pi}\right)^{3n/2}\left(1-\frac{n}{\widetilde{N}}\right)^{-3\widetilde{N}/2} e^{-3n/2} \sim \left(\frac{3\widetilde{N}}{2\pi}\right)^{3n/2}, \qquad (62.3)$$

whence, substituting into formula (62.2), we find

$$\rho(p, q, n) = \frac{1}{Qn!}\left[\frac{N/V}{(2m\pi T)^{3/2}}\right]^n e^{-E/T}.$$

It should be noted now that, according to formulae (40.5), (40.3) ($g = 1$, $a = h^3$), the factor $\frac{h^{3N}}{V(2\pi mT)^{3/2}}$ is equal to the exponential $e^{\mu_t/T}$, where μ_t is the chemical potential of an ideal gas (thermostat). But in the case of an equilibrium exchange of particles between the system and the thermostat $\mu_t = \mu$ (see Sec. 26), the chemical potential of the thermostat is equal to the chemical potential of the system, and we finally obtain the formula

$$\rho(p, q, n) = \frac{1}{n!\,h^{3n}} e^{(\mu n - E)/T} Q^{-1}, \qquad (62.4)$$

which represents the *Gibbs grand canonical distribution*. The quantity Q, called the statistical Q-integral, or Q-sum, is determined by the normalization condition

$$\sum_{n=0}^{\infty} \int d^{3n}p\, d^{3n}q\, \rho(p, q, n) = 1,$$

whence

$$Q(\mu, T) = \sum_{n=0}^{\infty} \frac{e^{\mu n/T}}{n!\,h^{3n}} \int d^{3n}p\, d^{3n}q e^{-E/T} = \sum_{n=0}^{\infty} \frac{e^{\mu n/T}}{n!\,h^{3n}} Z_n(T), \qquad (62.5)$$

where $Z_n(T)$ is the statistical Z-integral of Gibbs' canonical distribution for a system of n particles.

Let us finally derive the T-P-N distribution for the case when the number of system's particles is fixed, but in addition to energy, the volume of the system can fluctuate. The microcanonical distribution for the distribution function of the combined system is

$$\rho(p, q, v, P, Q, V) = \Lambda\delta\left(\sum_i \frac{P_i^2}{2m} + E - \widetilde{E}\right), \quad v + V = \widetilde{V}. \qquad (62.6)$$

Integrating over the coordinates and momenta of thermostat's particles, we obtain, in addition to constants and the Gibbs factor $e^{-E/T}$, the multiplier which depends on volume v of the system, $V^N = (\widetilde{V} - v)^N = \widetilde{V}^N\left(1 - \frac{v}{\widetilde{V}}\right)^N \approx \widetilde{V}^N\left(1 - \frac{v}{V_1}\right)^N$. Using the equation

of state $V = NT/P_t$ (where P_t is the thermostat pressure), we write down the variable multiplier in the form $\left(1-\frac{P_t v}{NT}\right)^N \approx e^{-P_t v/T}$, which is valid at $N \to \infty$.

Since the equilibrium condition for the system and the thermostat consists in the equality of pressures, $P_t = P$, we obtain the expression

$$\rho(p, q, v) = \frac{1}{X} e^{-(Pv+E)/T}, \tag{62.7}$$

representing the required T-P-N distribution. The quantity X is the set of all multipliers not containing v, and is referred to as the statistical X-integral. It is determined by the normalization condition

$$\int dv \int\int d^{3N}p\, d^{3N}q\rho(p, q, v) = 1$$

and is equal to

$$X = \int dv e^{-Pv/T} \int\int dp\, dq e^{-E(p, q, v)/T}. \tag{62.8}$$

63*. Another Derivation of the T-V-N, T-V-μ and T-P-N Distributions. Thermodynamic Corollaries

The statistical distributions for T-V-N, T-V-μ and T-P-N systems were derived in Secs. 61, 62, assuming the thermostat to be an ideal gas. In the case when, in addition to energy, the system exchanges with the thermostat also particles (T-V-μ system) this assumption essentially narrows the validity of the results obtained, since the nature of system's particles is restricted—they must be similar to the thermostat's particles. We shall consider, therefore, another, a more abstract but a more general derivation of the statistical distribution for a system of interacting particles, assuming that in this system the energy, the number of particles and the volume can fluctuate. The T-V-N, T-V-μ and T-P-N distributions will be subsequently obtained as particular cases.

The reasoning which we will used now mathematically resembles the box-and-cell method of derivation of the Maxwell-Boltzmann distribution, but the fundamental principles of the two methods differ radically.

We shall consider quantum-mechanical systems with quantized values of energies. In addition, for the sake of simplicity, the system volume V, just as the number of particles N and the energy E, will be assumed to acquire quantized discrete values—the transition from summation over the volume to integration will be carried out at the end of the derivation.

Introducing the concept of the probability density for the Gibbs canonical distribution, we have been examining many copies of the same system with the same number of particles and volumes (the Gibbs canonical ensemble). Let us consider now a wider ensemble consisting of copies of the same physical macroscopic system, differing from each other not only in the instantaneous states—phase trajectories, but also in the number of particles N and volume V. The energy of each copy depends on the complete set of quantum numbers determining the state of the system and, parametrically, on the number of system's particles and its volume. Denoting the complete set of quantum numbers by i, we have $E = E(i \mid N, V)$. The complete number of copies in the ensemble, L, is assumed to be rather great, $L \to \infty$.

Let us denote by $n[N, V, E(i \mid N, V)]$ the number of copies in the ensemble for which the number of particles, volume and energy acquire present values N, V, $E(i \mid N, V)$. The logical foundation of the derivation consists in the following. Let us replace mentally the interaction between the system and the thermostat, resulting in a change in energy, number of particles and volume of the system, by the interaction between the copies of the ensemble and the "large thermostat", assuming the gas of copies to be immersed in the "large thermostat". The states with fixed values of N, V and $E(i \mid N, V)$ will then play the same role as the cells in the Boltzmann method, and the number of copies $n[N, V, E(i \mid N, V)]$ the part of the number of molecules in the cells. It is clear that the concept of the box is not used here—there is only one box including all possible states of the gas of copies.

The number of ways in which the copies of the ensemble can be distributed among the cells is equal to

$$W = \frac{L!}{\prod\limits_{i, N, V} n[N, V, E(i \mid N, V)]!}. \tag{63.1}$$

The copies of the ensemble are assumed to be distinguishable, since not microparticles are concerned, obeying the quantum-mechanical indistinguishability principle, but macroscopic copies with different energies, numbers of particles, and volumes.

It will also be assumed that there exists a Gibbs microcanonical distribution for a gas of copies (just as in the preceding section the thermostat and the surroundings were assumed to form a closed system). Therefore, in addition to the complete number of copies L, the total number of particles in all copies $\tilde{N}$, the total volume of all copies $\tilde{V}$ and the total energy of all copies $\tilde{E}$ will be assumed fixed. Then, we have

$$\sum_N \sum_V \sum_i n[N, V, E(i \mid N, V)] = L \tag{63.2}$$

—the condition fixing the total number of copies in the ensemble,

$$\sum_N \sum_V \sum_i Nn[N, V, E(i|N, V)] = \tilde{N} \tag{63.3}$$

—the condition fixing the total number of particles in the ensemble,

$$\sum_N \sum_V \sum_i Vn[N, V, E(i|N, V)] = \tilde{V} \tag{63.4}$$

—the condition fixing the total volume of the ensemble,

$$\sum_N \sum_V \sum_i E(i|N, V)\, n[N, V, E(i|N, V) = \tilde{E} \tag{63.5}$$

—the condition fixing the total energy of the ensemble.

The fundamental postulate underlying the following derivation consists in that the most probable state of a real system (of one copy of the ensemble) with a predominant residence time can be identified with the most often encountered distribution of ensemble copies. In compliance with this postulate we must find the maximum of expression (63.1) (actually this can be easier done for the expression $\sigma = \ln W$) with account taken of the supplementary conditions (63.2) through (63.5). Using the Lagrangian method of multipliers and applying Sterling's formula, we look for the maximum of the expression

$$\Phi = \sigma + \alpha\tilde{N} - \gamma\tilde{V} - \beta\tilde{E} + (\delta + 1)\, L,$$

where

$$\sigma = \ln W = L \ln L - \sum_{N, V, i} n[N, V, E(i|N, V)] \ln n[N, V, E(i|N, V)].$$

Differentiating the n's as independent quantities and equating the first derivative of Φ to zero, we obtain

$$\ln n + \gamma V + \beta E - \alpha N - \delta = 0,$$

whence we find

$$n = \exp\,[\delta + \alpha N - \gamma V - \beta E\,(i \mid N, V)]. \tag{63.6}$$

The Lagrangian multiplier δ is found from formula (63.2)

$$e^{\delta} = \frac{L}{\sum\limits_{N, V, i} \exp\,[\alpha N - \gamma V - \beta E\,(i \mid N, V)]}, \tag{63.7}$$

and we obtain

$$\frac{n}{L} = \frac{\exp\,[\alpha N - \gamma V - \beta E\,(i \mid N, V)]}{Y(\alpha, \beta, \gamma)}, \tag{63.8}$$

where the quantity $Y(\alpha, \beta, \gamma)$, equal to

$$Y(\alpha, \beta, \gamma) = \sum_{i, N, V} \exp[\alpha N - \gamma V - \beta E(i \mid N, V)], \quad (63.9)$$

is called the *statistical Y-sum*. The quantities α, β, γ must be found from the conditions described by formulae (62.3) through (62.5). It should be noted that in contrast to Boltzmann's box-and-cell method no difficulties arise in the presented derivation associated with the use of Stirling's formula, since the numbers $n[N, V, E(i \mid N, V)]$ are proportional to the number of ensemble copies L, which can be assumed to be as large as desired.

The ratio $n/L = W[N, V, E(i \mid N, V)]$ is the probability that the system is in a state with the number of particles N, volume V and energy $E(i \mid N, V)$. If the energy level $E(i \mid N, V)$ is degenerate, the probability of the system being in any of the states with the number of particles N, volume V and energy $E(i \mid N, V)$ is obtained, multiplying the ratio n/L by the degeneracy $g(i \mid N, V)$:

$$W[N, V, E(i \mid N, V)] = g(i \mid N, V) \frac{\exp[\alpha N - \gamma V - \beta E(i \mid N, V)]}{\sum_{N, V, i} g(i \mid N, V) \exp[\alpha N - \gamma V - \beta E(i \mid N, V)]}. \quad (63.10)$$

The thermodynamic meaning of the parameters α, β, γ is discovered by introducing a physical postulate similar to the Boltzmann principle applied in the theory of ideal gases (Sec. 35). The expression $L^{-1} \ln W = \sigma/L$ will be identified with thermodynamic entropy

$$S = \frac{\sigma}{L}. \quad (63.11)$$

Just as for ideal gases, the grounds for such identification are, firstly, the additivity of the quantities S and σ and, secondly, the fact that the quantities S and σ reach their maximum values in the most probable state—equilibrium state from the viewpoint of thermodynamics. The need for dividing by L in formula (63.11) is associated with the fact that we determine the entropy of a real system, i.e. the entropy related to one copy of the ensemble. Substituting the value of σ and using Stirling's formula, we get

$$S = \frac{1}{L} \ln \left\{ \frac{L!}{\prod_{N, V, i} n[N, V, E(i \mid N, V)]!} \right\} = \frac{1}{L} \left[L \ln L - \sum_{N, V, i} n \ln n \right] = - \sum_{N, V, i} \frac{n}{L} \ln \left(\frac{n}{L} \right). \quad (63.12)$$

Formula (63.12) determines the entropy of arbitrary states of the system, both of equilibrium and non-equilibrium ones. Using for-

mula (63.8), we find in equilibrium state the entropy is

$$S = \ln [Y(\alpha, \beta, \gamma)] - \alpha \bar{N} + \gamma \bar{V} + \beta \bar{E},$$

where $\bar{N} = \tilde{N}/L$, $\bar{V} = \tilde{V}/L$, $\bar{E} = \tilde{E}/L$ are the mean values of the number of particles, volume and energy of the system*.

Let us consider now as particular cases the T-V-N, T-V-μ and T-P-N systems.

1. T = const, V = const, N = const. In this case the summation in formula (63.10) is carried out only over the set of quantum numbers i, the constant multiplier $e^{\alpha N - \gamma V}$ being taken out of the summation sign and eliminated together with the same multiplier in the numerator. Omitting the constant parameters N and V in the expression for the energy, we obtain

$$W(i) = g(i) \frac{e^{-\beta E(i)}}{Z(\beta)}, \tag{63.13}$$

where $W(i)$ is the probability that the system energy equals $E(i)$ and the partition function is equal to

$$Z(\beta) = \sum_i g(i) e^{-\beta E_i}. \tag{63.14}$$

The expression for mean energy $\bar{E}$ has the form

$$\bar{E} = \sum_i E(i) W(i) = \frac{1}{Z(\beta)} \sum_i E(i) g(i) e^{-\beta E(i)}, \tag{63.15}$$

or

$$\bar{E} = -\frac{\partial}{\partial \beta} [\ln Z(\beta)]. \tag{63.16}$$

For a T-V-N system the expression for the entropy (63.12) acquires the following form:

$$S = \left\{ \ln L - \sum_i \frac{g(i) e^{-\beta E(i)}}{Z} [\ln L - \ln Z - \beta E(i)] \right\}.$$

Upon summation, we obtain

$$S = \ln Z(\beta) + \beta \bar{E}. \tag{63.17}$$

To find the meaning of the parameter β, we calculate the differential of entropy, assuming N and V to be constant, and compare the result with the thermodynamic formula for dS. Differentiating

* To ensure uniform notation, we prefer not to denote in this section the internal energy by the symbol U, coinciding, by definition, with the mean energy. Similarly, the quantities $\bar{N}$ and $\bar{V}$ represent the number of particles N and the volume V in the thermodynamic sense.

Eq. (63.17) with respect to β, and using Eq. (63.16), we obtain

$$\left(\frac{\partial S}{\partial \beta}\right)_{N, V} = \beta \frac{\partial \bar{E}}{\partial \beta},$$

whence

$$(dS)_{N, V} = \beta (dE)_{N, V}.$$

On the other hand, in thermodynamics (see Sec. 19), $dU = d\bar{E} = T\,dS - P\,dV + \mu\,d\bar{N}$, whence $(dS)_{N,V} = \frac{1}{T} d\bar{E}$. Comparing the last two formulae, we obtain

$$\beta = \frac{1}{T}. \tag{63.18}$$

Let us now find the thermodynamic meaning of the function $Z(\beta)$. Substituting the value of β from (63.17), we get

$$\ln Z(\beta) = S - \frac{\bar{E}}{T} = -\frac{F(T, V, N)}{T}, \tag{63.19}$$

where $F = \bar{E} - TS$ is the free energy of the system. The expression for the probability (63.13) then becomes

$$W(i) = g(i) \exp \frac{F(T, V, N) - E(i)}{T}. \tag{63.20}$$

Formulae (63.13) and (63.20) express the Gibbs canonical distribution. The arguments of the free energy $F(T, V\ N)$ were indicated explicitly, to underline that the natural variables of free energy are precisely the parameters that are fixed for the Gibbs canonical ensemble.

2. $T = \text{const}$, $V = \text{const}$, $\mu = \text{const}$. Summation in formula (63.9) is performed over i and N and the factor $e^{-\gamma V}$ drops out of expression (63.10). Omitting the parameter V, we have

$$W(i, N) = g(i, N) \frac{\exp[\alpha N - \beta E(i \mid N)]}{Q(\alpha, \beta)}, \tag{63.21}$$

where $W(i, N)$ is the probability that the system contains N particles and its energy is $E(i \mid N)$, and the partition function is expressed by the formula

$$Q(\alpha, \beta) = \sum_{i, N} g(i, N) \exp[\alpha N - \beta E(i \mid N)]. \tag{63.22}$$

The internal energy of the system equals

$$\bar{E} = \sum_{i, N} E(i \mid N) W(i, N) = \sum_{i, N} g(i, N) E(i, N) \frac{\exp[\alpha N - \beta E(i \mid N)]}{Q(\alpha, \beta)}, \tag{63.23}$$

or

$$\overline{E} = -\frac{\partial}{\partial \beta}[\ln Q(\alpha, \beta)], \tag{63.24}$$

and the average number of particles in the system, $\overline{N}$, is expressed by the formula

$$\overline{N} = \sum_{i, N} NW(i, N) = \frac{\sum_{i, N} g(i, N) N \exp[\alpha N - \beta E(i \mid N)]}{Q(\alpha, \beta)}, \tag{63.25}$$

or

$$\overline{N} = \frac{\partial}{\partial \alpha}[\ln Q(\alpha, \beta)]. \tag{63.26}$$

The expression for the entropy S for a T-V-μ system has the following form:

$$S = \ln L - \sum_{i, N} \frac{\exp[\alpha N - \beta E(i \mid N)]}{Q(\alpha, \beta)} (\ln L - \ln Q + \alpha N - \beta E).$$

Summing up and using formulae (63.23) and (63.26), we obtain

$$S = \ln Q(\alpha, \beta) - \alpha \overline{N} + \beta \overline{E}. \tag{63.27}$$

To elucidate the thermodynamic meaning of the parameter α, we find the differential of the entropy at $V = \text{const}$ and compare it with the corresponding thermodynamic formula. Differentiating Eq. (63.27) with respect to α at $\beta = \text{const}$, $V = \text{const}$ and with respect to β at $\alpha = \text{const}$, $V = \text{const}$, and allowing for formulae (63.24) and (63.26), we obtain

$$\left(\frac{\partial S}{\partial \alpha}\right)_{\beta, V} = -\alpha \frac{\partial \overline{N}}{\partial \alpha} + \beta \frac{\partial \overline{E}}{\partial \alpha}, \tag{63.28}$$

$$\left(\frac{\partial S}{\partial \beta}\right)_{\alpha, V} = -\alpha \frac{\partial \overline{N}}{\partial \beta} + \beta \frac{\partial \overline{E}}{\partial \beta}. \tag{63.29}$$

Multiplying (63.28) by $d\alpha$, (63.29) by $d\beta$ and summing up the results obtained, we get

$$(dS)_V = -\alpha (d\overline{N})_V + \beta (d\overline{E})_V.$$

Comparing with the thermodynamic formula

$$(dS)_V = \frac{1}{T}(d\overline{E})_V - \frac{\mu}{T}(d\overline{N})_V,$$

we find that

$$\beta = \frac{1}{T}, \quad \alpha = \frac{\mu}{T}. \tag{63.30}$$

Substituting the values of α and β into formula (63.27), we find

$$\ln Q(\alpha, \beta) = S + \frac{\mu\bar{N} - \bar{E}}{T}.$$

By virtue of the thermodynamic formulae $\mu\bar{N} = \Phi = \bar{E} - TS + p\bar{V}$ and $\Omega = -P\bar{V}$ it follows that

$$\ln Q(\alpha, \beta) = -\frac{\Omega(T, V, \mu)}{T}, \tag{63.31}$$

$$Q = \exp\left[-\frac{\Omega(T, V, \mu)}{T}\right]. \tag{63.32}$$

Then the expression for the probability acquires the form

$$W(i, N) = g(i, N) \exp\frac{1}{T}[\Omega(T, V, \mu) + \mu N - E(i \mid N)]. \tag{63.33}$$

Formula (63.33) expresses the Gibbs grand canonical distribution. It should again be emphasized that the "own" variables of the Ω-potential, T, V, μ, are precisely the parameters that are fixed for the Gibbs grand canonical ensemble.

3. $T = \text{const}$, $P = \text{const}$, $N = \text{const}$. In this case summation in formula (63.9) is performed over i and over the volume, and the factor $e^{\alpha N}$ drops out of the distribution. Passing to a continuously varying volume, we can write formula (63.10) in the form

$$dW(i, V) = \frac{\exp[-\beta E(i \mid V) - \gamma V]}{X(\beta, \gamma)} g(i, V)\, dV, \tag{63.34}$$

where the quantity $dW(i, V)$ is the probability that the volume of the system lies in the range V, $V + dV$ and that the system energy is equal to $E(i, V)$; the quantity $g(i, V)\, dV$ in the formula is the multiplicity of the energy level $E(i \mid V)$ for the same range of the system volume, and the integral of states $X(\beta, \gamma)$ is expressed by the formula

$$X(\beta, \gamma) = \int \sum_i \exp[-\beta E(i \mid V) - \gamma V]\, g(i, V)\, dV. \tag{63.35}$$

The mean energy, as before, is specified by the formula

$$\bar{E} = -\frac{\partial}{\partial\beta} \ln X(\beta, \gamma), \tag{63.36}$$

and the mean volume of the system

$$\bar{V} = \int \sum_i V\, dW(i, V)$$

$$= X^{-1}(\beta, \gamma) \int \sum_i V \exp[-\beta E(i \mid V) - \gamma V]\, g(i, V)\, dV, \tag{63.37}$$

or

$$\overline{V} = -\frac{\partial}{\partial \gamma}[\ln X(\beta, \gamma)]. \tag{63.38}$$

Let us find the entropy of the T-P-N system:

$$S = \ln L - \int \sum_i \frac{\exp[-\gamma V - \beta E(i \mid V)]}{X(\beta, \gamma)} \times [\ln L - \ln X - \gamma V - \beta E]\, g(i, V)\, dV.$$

Summing up and integrating, and using the definitions of energy $\overline{E}$ and volume $\overline{V}$, we obtain

$$S = \ln X(\beta, \gamma) + \gamma \overline{V} + \beta \overline{E}. \tag{63.39}$$

To clarify the thermodynamic meaning of the coefficient γ, we again find the differential dS at a constant N and compare the result with the corresponding thermodynamic expression. Differentiating Eq. (63.39) with respect to γ and β and allowing for formulae (63.36) and (63.38), we find

$$\left(\frac{\partial S}{\partial \gamma}\right)_{N, \beta} = \gamma \left(\frac{\partial \overline{V}}{\partial \gamma}\right)_{N, \beta} + \beta \left(\frac{\partial \overline{E}}{\partial \gamma}\right)_{N, \beta},$$

$$\left(\frac{\partial S}{\partial \beta}\right)_{N, \gamma} = \gamma \left(\frac{\partial \overline{V}}{\partial \beta}\right)_{N, \gamma} + \beta \left(\frac{\partial \overline{E}}{\partial \beta}\right)_{N, \gamma},$$

whence

$$(dS)_N = \gamma\, (d\overline{V})_N + \beta\, (d\overline{E})_N. \tag{63.40}$$

Comparing with the thermodynamic formula

$$(dS)_N = \frac{P}{T}(d\overline{V})_N + \frac{1}{T}(d\overline{E})_N, \tag{63.41}$$

we find by analogy with (63.30) that

$$\beta = \frac{1}{T}, \quad \gamma = \frac{P}{T}. \tag{63.42}$$

Substituting the values of γ and β into formula (63.39), we obtain

$$\ln X(\beta, \gamma) = S - \frac{P\overline{V} + \overline{E}}{T} = -\frac{\Phi(T, P, N)}{T}, \tag{63.43}$$

$$X = \exp\left[-\frac{\Phi(T, P, N)}{T}\right]. \tag{63.44}$$

Thus, for a T-P-N system the expression for the probability acquires the following form:

$$dW(i, V) = \exp \frac{\Phi(T, P, N) - PV - E(i \mid V)}{T} g(i, V)\, dV. \tag{63.45}$$

The natural variables of the thermodynamic potential, T, P, N, are precisely the parameters fixed in the T-P-N ensemble.

4. T = const, P = const, μ = const. The system can exchange particles with the thermostat and change its volume. Let us find the Y-sum for this system. Substituting the values of the parameters α, β, γ into formula (63.13), we obtain

$$\ln Y = S + \frac{\mu\bar{N} - P\bar{V} - \bar{E}}{T} = 0. \tag{63.46}$$

Here the account was taken of the fact that $\mu\bar{N} = \Phi = \bar{E} - TS + P\bar{V}$. Therefore for this case the expression of the distribution becomes

$$dW(i, N, V) = \exp\frac{\mu N - PV - E(i, N, V)}{T}\, g(i, N, V)\, dV. \tag{63.47}$$

In spite of the fact that no use will be made of the distribution (63.47), we consider it useful to draw the reader's attention to the following seeming contradiction.

Formula (63.47) could be used to derive the following expressions for the mean energy, number of particles and volume:

$$\bar{E} = -\left(\frac{\partial Y}{\partial \beta}\right)_{\alpha, \gamma}, \quad \bar{N} = \left(\frac{\partial Y}{\partial \alpha}\right)_{\beta, \gamma}, \quad \bar{V} = \left(\frac{\partial Y}{\partial \gamma}\right)_{\alpha, \beta} \tag{63.48}$$

However, as can be seen from (63.46), $Y = 1$ = const. The clue to this paradox is that the conditions T = const, P = const, μ = = const are not satisfied at any values of T, P, μ. In an equilibrium state the intensive parameters T, P, μ are related by the expression $\mu = \mu(T, P)$ which is equivalent to the equality $Y(\alpha, \beta, \gamma) = 1$. To apply formula (63.48), it is necessary to calculate the Y-sum by formula (63.9), assuming α, β, γ arbitrary, and make use of relationship $\mu = \mu(T, P)$ [or $Y(\alpha, \beta, \gamma) = 1$] only after the derivatives in formula (63.48) have been calculated.

In concluding this section, let us sum up the results obtained in the two last sections.

There are three pairs of conjugated variables: T, S; P, V and μ, N. The behaviour of the system is considered under conditions when one parameter in each pair is fixed. We shall consider systems immersed into a thermostat and assume that of the first pair of variables temperature is fixed in all the cases. Selecting in different ways the fixed parameters in the second P, V and third μ, N pairs we naturally arrive at T-V-N, T-V-μ, T-P-N and T-P-μ systems.

Given below are the main formulae for each of the four cases.

T-V-N system:

$$W(i) = \frac{\exp[-E(i)/T]}{Z} g(i) = \exp\left[\frac{F(T, V, N) - E(i)}{T}\right] g(i),$$

$$Z = \sum_i \exp\left[-\frac{E(i)}{T}\right] g(i) = \exp\left[-\frac{F(T, V, N)}{T}\right], \quad (63.49)$$

$$\bar{E} = -\frac{\partial}{\partial \beta}(\ln Z) = T^2 \frac{\partial}{\partial T}(\ln Z)$$

T-V-μ system:

$$W(i, N) = \frac{\exp[\mu N - E(i \mid N)/T]}{Q} g(i, N)$$

$$= \exp\left[\frac{\Omega(T, V, \mu) + \mu N - E(i \mid N)}{T}\right] g(i, N),$$

$$Q = \sum_{i, N} \exp\left[\frac{\mu N - E(i \mid N)}{T}\right] g(i, N) = \exp\left[-\frac{\Omega(T, V, \mu)}{T}\right], \quad (63.50)$$

$$\bar{E} = -\frac{\partial}{\partial \beta}(\ln Q)_\alpha = T^2 \frac{\partial}{\partial T}(\ln Q)_{\mu/T}, \quad \bar{N} = \frac{\partial}{\partial \alpha}(\ln Q)_\beta = T \frac{\partial}{\partial \mu}(\ln Q)_T.$$

T-P-N system:

$$dW(i, V) = \exp\left[\frac{PV + E(i \mid V)}{T}\right] g(i, V)\, dV$$

$$= \exp\left[\frac{\Phi(T, P, N) - PV - E(i \mid V)}{T}\right] g(i, V)\, dV,$$

$$X = \int \sum_i \exp\left[-\frac{PV + E(i \mid V)}{T}\right] g(i, V)\, dV = \exp\left[-\frac{\Phi(T, P, N)}{T}\right]. \quad (63.51)$$

$$\bar{E} = -\frac{\partial}{\partial \beta}(\ln X)_\gamma = T^2 \frac{\partial}{\partial T}(\ln X)_{P/T},$$

$$\bar{V} = -\frac{\partial}{\partial \gamma}(\ln X)_\beta = -T \frac{\partial}{\partial P}(\ln X)_T.$$

T-P-μ system:

$$dW(i, N, V) = \exp\left[\frac{\mu N - PV - E(i \mid N, V)}{T}\right] g(i, N, V)\, dV. \quad (63.52)$$

It should be noted that if the fluctuations of the number of particles and volume are ignored, and N is replaced by $\bar{N}$ and V by $\bar{V}$, in all four distributions the term $E(i \mid N, V)$ in the exponent is preceded by the free energy expressed in different variables; this stems directly from the thermodynamic formulae (see Sec. 19) $F = \Omega + \mu\bar{N} = \Phi - P\bar{V}$. It follows that when the fluctuations of the number of particles and volume are of no interest for us, the four

distributions become equivalent and the selection of the distributions for the solution of a particular problem is determined only by mathematical considerations.

It should also be noted that for the T-V-μ, T-P-N and T-P-μ systems the energy-, volume- and number-of-particle distributions have sharp maxima, just as the energy distribution for the T-V-N system (see Sec. 62). For this reason the probabilities of large fluctuations of the number of particles N and volume V are very small. This makes the equivalence of the distributions under consideration completely evident.

Not temperature but entropy could be assumed fixed in the pair of conjugate variables (T, S); then a system should be placed into an ideally heat-insulated vessel and not into a thermostat. In this case two parameters for the pairs (P, V) and (μ, N) can be fixed in four ways. However, the most realistic is the case when S, V and N are constant. Physically, such a system should be imagined placed into a vessel with fixed (V = const) ideally heat-insulated walls (S = const), impermeable for system's particles (N = const). In this situation the system is completely isolated from the surroundings and its energy is constant. We then obtain the Gibbs microcanonical distribution (see Sec. 61)

$$\rho(E_i, N, V) = \Lambda\delta(E_i - \widetilde{E})\,\delta(V - \widetilde{V})\,\delta_{\widetilde{N}, N}. \tag{63.53}$$

Let us consider now the transition to a classical description with continuously varying energy. This transition must be carried out by replacing the quantities $g(i)$, $g(i, N)$, $g(i, V)$ by the quantity $\frac{d\Gamma_N}{h^{3N}N!}$, where $d\Gamma_N = \prod_{i=1}^{3N} dp_i dq_i$. Then the summation over i in the expressions for $Z(T)$, $Q(\mu, T)$, $X(P, T)$ must be replaced by integration over $d\Gamma_N$, and we obtain

$$Z = \frac{1}{h^{3N}N!} \int e^{-E(p, q)/T}\, d\Gamma_N, \tag{63.54}$$

$$Q = \sum_N \frac{e^{\mu N/T}}{h^{3N}N!} \int e^{-E(p, q|N)/T}\, d\Gamma_N, \tag{63.55}$$

$$X = \int dV\, \frac{e^{-PV/T}}{h^{3N}N!} \int e^{-E(p, q|V)/T}\, d\Gamma_N. \tag{63.56}$$

The energy $E(p, q/V)$ in formula (63.56) and the integration limits in the integral depend on V.

The appearance of the factor $N!$ in the denominators of expressions (63.54) through (63.56) is motivated as follows. By virtue of the

particle indistinguishability principle of quantum mechanics (symmetry or antisymmetry of wave functions) the states, differing from each other by particle permutations, must be considered as the same state. This is accounted for automatically by the summation over the energy levels in the expressions for Z, Q and X. When passing to integration over the Γ-space, however, we must either integrate not over the entire Γ-space (the points of Γ-space differing by permutations of the coordinates and momenta with each other should not be considered as different points), or if we integrate over all values of p_i, q_i independently, then the error introduced must be compensated for by dividing by the total number of permutations of N molecules, equal to $N!$

Note that notwithstanding the seeming likeness and the undoubtedly existing relation between this method and the artificial Gibbs method, applied in the ideal gas theory (Sec. 36), the two methods differ in principle. The Gibbs method was applied within the framework of the Maxwell-Boltzmann distribution, based on the erroneous hypothesis on the distinguishability of microparticles and having the meaning only as the extreme case of the correct Fermi-Dirac and Bose-Einstein equations. As was already emphasized the Gibbs method is logically erroneous.

By contrast, the method described here is not based on any physical hypothesis and is applied within the framework of exact statistical distributions, the canonical, grand canonical, etc. It is a purely mathematical method, simplifying the calculation of integrals over the Γ-space without singling out in it physically equivalent regions. It should be noted that for the T-V-N and T-P-N systems, for which $N = \text{const}$, the factor $(N!)^{-1}$ is constant and its presence is of no importance. For a T-P-μ system, however, this factor becomes essential and connot be omitted.

It will be shown, finally, that the Nernst theorem, proved in Sec. 39 for ideal gases, is also valid for systems of interacting particles. We shall limit ourselves for the sake of simplicity to considering the T-V-N system. According to formulae (63.11) and (63.1), the entropy of the system is equal to

$$S = \frac{1}{L} \ln W = \frac{1}{L} \ln \frac{L!}{\prod\limits_i n\,[E\,(i)]!}. \tag{63.57}$$

If the ground state of the system $i = 1$ is not degenerate, then at $T \to 0$ all copies of the system are in the ground state. This means that all $n\,[E\,(i)] = 0$, except $n\,[E\,(1)] = L$, and the entropy $S = 0$. If the ground state is degenerate with a degeneracy g, then as $T \to 0$, $n\,[E\,(i)] = L/g$ for $i = 1, 2, \ldots, g$ and $n\,[E\,(i)] = 0$ for $i > g$. Using Stirling's formula, we find then from Eq. (63.57) that $S \to \ln g = \text{const}$.

The following important remark should, however, be made, concerning Nernst's theorem. The proof based on formula (63.57), just as the proof for ideal gases discussed in Sec. 39, pertains to the region of rather low temperatures $T \ll E_1$, where E_1 is the first excited level of the system. For a system placed in a box with impermeable walls, for instance, $E_1 \propto \frac{h^2}{8mL^2}$ (see Sec. 45) and even at $L = 0.1$ cm the characteristic temperature $T_t \sim 10^{-10}$ K.

The entropy was shown experimentally to tend to the maximum constant value at considerably higher temperatures—of the order of one or tenths of kelvin. This is associated with the fact that for macroscopic bodies the energy spectrum is pratically almost continuous and the manner in which the entropy tends to its limiting value is determined by the behaviour of the density of states $\rho(E)$ in the neighbourhood of $E = 0$. For crystals, for instance, according to Debye's theorem (see Sec. 53), the entropy tends to zero according to the T^3-law at temperatures that are low compared to Debye's characteristic temperature, i.e., at $T \sim$ (0.1 to 1.0) K.

Problems

1. N molecules of an ideal gas are confined within a vessel of volume V. Let us consider a volume $v \ll V$. Apply the T-V-μ distribution to the molecules of the volume and prove the Poisson formula for the probability P_n that the volume v contains n molecules, $P_n = (\bar{n})^n e^{-\bar{n}}/n!$, where $\bar{n} = Nv/V$.
2. An ideal gas is in contact with an adsorbing surface having N adsorption centres. The energy of an adsorbed molecule is ε_0. Using the T-V-μ distribution, calculate the adsorption coefficient α—the ratio of the number of adsorbed molecules to N—as a function of pressure and temperature, i.e. obtain the formula for the *Langmuir isotherm*.

Answer. $\alpha = \dfrac{P}{P + (2\pi m/h^2)^{3/2} T^{5/2} e^{-\varepsilon_0/T}}$.

64. Derivation of the Bose-Einstein and Fermi-Dirac Distributions with the Aid of a Grand Canonical Ensemble

In this section we shall give the derivation of the Bose-Einstein and Fermi-Dirac distributions for ideal gases, not based on the assumption that $g_i \gg 1$.

Let us calculate for this purpose the Q-sum over states of an ideal gas. According to formulae (63.50),

$$Q = \sum_{N,\, i} \exp\left[\frac{\mu N - E\,(i \mid N)}{T}\right] g\,(i,\, N). \tag{64.1}$$

Let ε_k represent the possible energy values of one gas particle. The total energy of the ideal gas under consideration, E, and the total number of particles N can be expressed as follows:

$$E = \sum_k{}^{*} n_k \varepsilon_k, \quad N = \sum_k{}^{*} n_k, \tag{64.2}$$

where the symbol $\sum_k^{*}$ denotes the summation not over the energy levels but over various states of the particle, so that if the energy level ε_k is degenerate with a degeneracy g_k, then the term containing ε_k is repeated g_k times in the sums of formula (64.2).

Thus, in formula (64.1) the role of the parameter i is played by the set of n_k numbers for all states, $i \to \{n_1, n_2, \ldots\}$. In formula (64.1) the degeneracy for the entire gas, $g\,(i, N)$, must be assumed equal to unity, since assigning all the numbers n_k unambiguously determines the state of the gas. Hence,

$$Q = \sum_{N=0}^{\infty} \sum_{n_1+n_2+\ldots=N} \exp\left[\frac{\mu N - E}{T}\right]$$

$$= \sum_{N=0}^{\infty} \sum_{n_1+n_2+\ldots=N} \exp\left[\frac{\mu\,(n_1+n_2+\ldots)-(\varepsilon_1 n_1+\varepsilon_2 n_2+\ldots)}{T}\right]. \tag{64.3}$$

It should be noted that owing to the summation over N expression (64.3) includes all kinds of sets of numbers n_i with any value of $n_1 + n_2 + \ldots$, and the Q-sum can be rewritten to read

$$Q = \sum_{n_1} \sum_{n_2} \ldots e^{(\mu-\varepsilon_1)n_1/T} e^{(\mu-\varepsilon_2)n_2/T} \ldots \tag{64.4}$$

It can readily be seen that each term in (64.3) appears only once in (64.4); and vice versa, each term in (64.4) appears only once in sum (64.3), so that the two sums are equivalent. Finally, (64.4) can be presented as the product over all the levels:

$$Q = \prod_i \sum_{n_i} \exp\left[\frac{(\mu - \varepsilon_i)\, n_i}{T}\right]. \tag{64.5}$$

Let us now consider separately the cases involving the Bose- and Fermi gases.

In the case of a boson system the numbers n_i can take all values $n = 0, 1, 2, \ldots$, and, finding the sum of the geometrical progres-

sion, we obtain

$$\sum_{n_i=0}^{\infty} [e^{(\mu-\varepsilon_i)/T}]^{n_i} = \frac{1}{1-e^{(\mu-\varepsilon_i)/T}},$$

whence

$$Q = \prod_i [1 - e^{(\mu-\varepsilon_i)/T}]^{-1}. \tag{64.6}$$

In the case of a fermion system the numbers n_i take only two values $n_i = 0, 1$, and we have

$$Q = \prod_i [1 + e^{(\mu-\varepsilon_i)/T}]. \tag{64.7}$$

Since the Ω-potential of a gas is defined by formula (63.31) as $\Omega = -T \ln Q$, we obtain the expression

$$\Omega = \pm T \sum_i \ln [1 \mp e^{(\mu-\varepsilon_i)/T}], \tag{64.8}$$

valid for the boson gas (upper signs) and fermion gas (lower signs), i.e. we obtain formula (38.10).

Differentiating with respect to the chemical potential, we find

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} = \sum_i \frac{1}{e^{(\varepsilon_i-\mu)/T} \mp 1},$$

or in the case when the g_i energy levels merge into one level,

$$N = \sum_i \frac{g_i}{e^{(\varepsilon_i-\mu)/T} \mp 1},$$

whence for partial occupation numbers N_i we obtain

$$N_i = \frac{g_i}{e^{(\varepsilon_i-\mu)/T} \mp 1},$$

i.e. the basic formulae describing the Bose-Einstein and Fermi-Dirac distributions respectively.

Problems

1. Using the T-V-μ distribution, calculate the chemical potential, occupation numbers, energy, and heat capacity of an ideal gas with two energy levels $\varepsilon_0 = 0$, $\varepsilon_1 = \varepsilon$ and similar degeneracies $g_0 = g_1 = 1$ in the cases of fermions and bosons.
2. Examine the solution of Problem 1 with the aid of the T-V-N distribution.

65. Nonideal Gases

This section is devoted to the behaviour of a monoatomic gas for which atomic interaction cannot be ignored. The potential energy of atomic interaction will be assumed equal to the sum of the energies of pairwise interactions, depending only on interatomic distances:

$$\mathcal{U}_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_{i<k=2}^{N} \mathcal{U}(|\mathbf{r}_i - \mathbf{r}_k|). \tag{65.1}$$

The potential energy of pairwise atomic interaction possesses the following properties (Fig. 81). At $r = |r_i - r_k| > r_0$ predominating are the van der Waals attraction forces that diminish rapidly with distance. In quantum mechanics it is proved in rather general assumptions that in this region $\mathcal{U}(r) \propto r^{-6}$. Therefore at values of r considerable greater than r_0, $\mathcal{U}(r) < 0$, and the value $-\mathcal{U}(r)/T \ll 1$. At $r < r_0$ the rapidly increasing repulsive forces dominate, which are associated with the deformation of electron shells. Below, we shall assume $\mathcal{U}(r) \to \infty$ in a rough hard-sphere approximation. At $r = r_0$ (r_0 approximately represents the atomic diameter) the attraction and repulsive forces are balanced, and the potential energy of interaction is minimum.

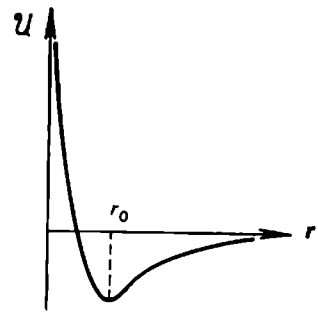


FIG. 81

We shall depart from the formula relating the Ω-potential of gas with the Q-sum over states [see Eqs. (62.5) and (63.31)].

$$e^{-\Omega/T} = Q = \sum_{N=0}^{\infty} e^{\mu N/T} \sum_i e^{-E(i|N)/T} g(i, N). \tag{65.2}$$

To derive the equation of state of a nonideal gas, it is sufficient to consider the translational motion of its atoms, ignoring all internal degrees of freedom. Consequently, the quantization of energy levels is immaterial, and we shall turn to a classical description, replacing the degeneracy $g(i, N)$ by the expression

$$\frac{d\Gamma_N}{h^{3N} N!} = \frac{\prod_i d^3 r_i \, d^3 p_i}{h^{3N} N!},$$

and the energy $E(i \mid N)$ by the expressions

$$E_0(p, \mathbf{r}) = 0, \quad E_1(p, \mathbf{r}) = \frac{p^2}{2m}, \tag{65.3}$$

$$E_N(p, \mathbf{r}) = \sum_{k=1}^{N} \frac{p_k^2}{2m} + \mathcal{U}_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N), \quad N \geqslant 2.$$

Integrating over the momenta, we obtain

$$Q(z, V, \beta) = \sum_{n=0}^{\infty} \left(\frac{z}{\lambda^3}\right)^n \frac{Z_n(V, \beta)}{n!}, \tag{65.4}$$

where $z = e^{\beta\mu}$ *activity*;

$\lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2}$ = de Broglie wavelength, corresponding to the mean thermal energy;

$\beta = 1/T$,

and

$$Z_n(V, \beta) = \int \ldots \int d^3r_1 \ldots d^3r_n \exp\left[-\beta \sum_{i<k}^{n} \mathcal{U}(r_{ik})\right]$$

is a configurational integral.

Let us introduce the quantities

$$f_{ik} = e^{-\beta \mathcal{U}(r_{ik})} - 1 \tag{65.5}$$

the *Mayer functions*. In accordance with the properties of the potential energy of molecular interaction $\mathcal{U}(r_{ik})$, the quantities f_{ik} become very small at $r_{ik} > r_0$, tend to -1 at $r_{ik} \approx r_0$ and are bounded in the region of intermediate molecular distances. On the introduction of the quantities f_{ik} the expression for the configurational integral acquires the form

$$Z_n(V, T) = \int \ldots \int d^3r_1 d^3r_2 \ldots d^3r_n \prod_{i<k=2}^{n} (1 + f_{ik})$$

$$= \int \ldots \int d^3r_1 \ldots d^3r_n [1 + (f_{12} + f_{13} + \ldots + f_{n-1,n}) + (f_{12}f_{13} \ldots) + \ldots]. \tag{65.6}$$

It is especially convenient to expand the integrand in powers of Mayer's functions f_{ik} in expression (65.6) to consider the behaviour of rarefied gases. The fact is that each multiplier f_{ik} limits effectively one of the integrations in the integral $\int d^3r_i\, d^3r_k$ to a volume of the order of r_0^3 and, consequently, compared with the integral not containing

f_{ik}, contributes to the result the small multiplier r_0^3/V. This means that different regions of the configurational space contribute to different terms in formula (65.6). The entire configurational space contributes to the integral $\int d^3r_1\, d^3r_2 \ldots d^3r_n$, corresponding to the term 1 in the square brackets. Only those regions of the configurational space for which $|\mathbf{r}_l - \mathbf{r}_k| \leqslant r_0$, i.e. where the collision of two molecules occurred, contribute to the integral containing the factor $\sum f_{ik}$. To the integral containing the factor $\sum f_{ik}f_{jl}$ a contribution is made by regions of the configurational space, corresponding to a triple molecular collision, when one of the indices j or l coincides with one of the indices i or k, or to a simultaneous collision of two pairs of molecules (the ith with the kth and the jth with the lth), etc.

Since in a rarefied gas collisions of molecular clusters consisting of a great number of molecules occur seldom, it is intuitively clear that expansion (65.6) must converge more or less rapidly.

The structure of the expansion (65.6) can be visually studied by comparing each term of this expansion with a diagram, generally referred to as a *graph*. Each variable $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ will be represented by a labeled circle, and each factor f_{ik} by a line segment drawn between the ith and the kth circles. The integral $\int d^3r_1 \ldots d^3r_6 f_{12}f_{24}f_{56}$, for instance, is represented by the graph depicted in Fig. 82. It is sufficient for our purposes to consider only the graphs in which only one line segment connects two circles, i.e. simple graphs. It is clear that expression (65.6) is represented by the sum of all kinds of graphs built up of N circles—N-particle graphs. In this case the first term in the square brackets is represented by the graph without segments between the circles, the second term of the expansion $(f_{12} + f_{13} + \ldots)$ is represented by $n(n-1)/2$ graphs with one line segment between the circles, the third term $(f_{12}f_{13} + \ldots)$ by the graphs with two segments between the circles, etc. Graphs can also be subdivided into *connected graphs*, i.e. graphs in which all circles are connected to one another directly or indirectly (through other circles), and *non-connected graphs* in which there are groups of circles or individual circles isolated from each other. For instance, the graph depicted in Fig. 83 (*a*) is a connected graph, the graph in Fig. 83 (*b*) a 2-connected graph and in Fig. 83 (*c*) a 3-connected graph, etc.

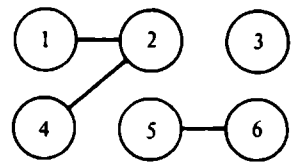


FIG. 82

Since each graph is juxtaposed unambiguously with an integral and each integral with a graph, for the sake of simplicity the word "graph" will often be used below instead of "integral", and we shall

speak of the sum or product of graphs instead of the sum or product of corresponding integrals.

It is clear that any integral corresponding to a k-connected graph breaks up into the product of integrals of a lower multiplicity. For

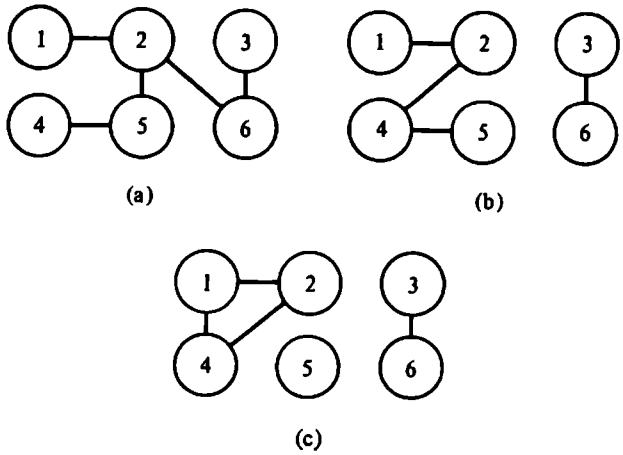


FIG. 83

instance, the integral corresponding to the graph depicted in Fig. 83 (b) is equal to

$$\int d^3r_1\, d^3r_2\, d^3r_4\, d^3r_5 f_{12} f_{24} f_{45} \int d^3r_3\, d^3r_6 f_{36},$$

and the integral corresponding to the graph in Fig. 83 (c) is equal to

$$\int d^3r_1\, d^3r_2\, d^3r_4 f_{12} f_{24} f_{14} \int d^3r_5 \int d^3r_3\, d^3r_6 f_{36}.$$

Let us call any k-particle connected graph a *k-group* and introduce the concept of the *group integral* $b_k(V, T)$, defining it as the product of the normalizing factor $1/k!\, V\lambda^{3k-3}$ and the sum of integrals corresponding to different k-groups. In this definition, by the different k-groups are assumed both the graphs, differing from one another in the number and arrangement of the lines between circles, and the graphs, differing in the labeling of circles with and without the lines between them. So, with $k = 3$ there exist four different 3-groups illustrated in Fig. 84. With $k = 4$ there exist 38 different 4-groups. Figure 85 shows 13 types of essentially different 4-groups that cannot be obtained from each other by rotating the figure in its plane. Figure 85 (a)-(e) depicts the groups with three lines between circles (also referred to as articulation points), Fig. 85 (f)-(j) the groups with four

lines between circles, Fig. 85 (k)-(l) the groups with five lines between circles, and Fig. 85 (m) the group with six lines between circles. The figures above the diagrams indicate the number of groups, differing

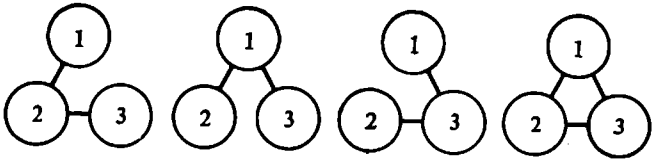


FIG. 84

in the labeling of circles with and without lines between them, including the group shown in the figure, can be obtained from the given picture by rotating it in its plane (the labels 1, 2, 3, 4 remain at their places during such rotation). So, three more equivalent graphs can

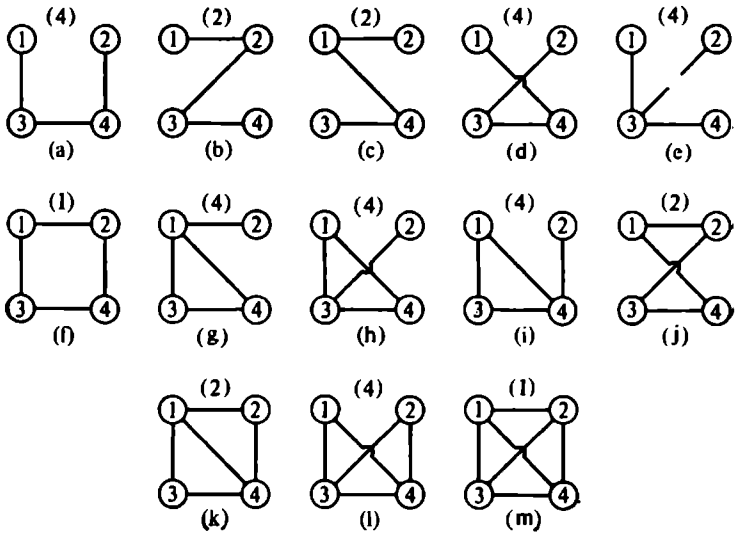


FIG. 85

be obtained from the graph depicted in Fig. 85 (a) by rotating the figure through 90°, 180°, 270°, and from the graph in Fig. 85 (b)—one more equivalent graph, by rotating the figure through 90°; the graphs shown in Fig. 85 (f) and Fig. 85 (m) are invariant in respect to rotation through 90°, and each of them determines only 4-group, etc.

The group integrals possess two important properties. Firstly, it is clear that $b_k(V, T)$ is a dimensionless quantity. Secondly, the quan-

tity $b_k(V, T)$ has a finite limit at $V \to \infty$, since of the k integrations only one is carried out over the entire volume V. The remaining $k-1$ integrations for the connected graphs are effectively limited by the region of volume $\propto r_0^3$, since all factors $f_{lm} \to 0$ at $r_{lm} \gg r_0$.

At $k = 1$ the graph ① is a 1-group and, accordingly,

$$b_1 = \frac{1}{V} \int d^3 r_1 = 1. \tag{65.7}$$

The graph ①-② is a 2-group and

$$b_2 = \frac{1}{2! V \lambda^3} \int d^3 r_1 \, d^3 r_2 f_{12} = \frac{1}{2! \lambda^3} \int d^3 r_{12} f_{12}(r_{12}) \tag{65.8}$$

(we passed to integration over the coordinates of the centre of inertia $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and the relative radius vector $\mathbf{r}_{12}$).

Four different 3-groups are shown in Fig. 84, and the group integral b_3 is equal to

$$b_3 = \frac{1}{3! V \lambda^6} \int d^3 r_1 \, d^3 r_2 \, d^3 r_3 [f_{12} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{23} f_{13}]. \tag{65.9}$$

Any n-particle graph is the product of several groups with a number of circles not exceeding n. If the number of k-groups is m_k, then we have the relationship

$$\sum_{k=1}^{n} k m_k = n. \tag{65.10}$$

It is clear then that $m_n \leqslant 1$, and if $m_n = 1$, all the remaining $m_k = 0$ ($k \neq n$). We then obtain a connected n-particle graph.

The given set of numbers m_k determines not a single n-particle graph, but a set of such graphs, since, firstly, at $k \geqslant 3$ the k-particle graphs can differ from one another (Figs. 84, 85) and, secondly, the labels of the variables $r_1, r_2, \ldots, r_n$ can be distributed differently among the groups.

Let us denote by $S(m_k)$ the sum of integrals juxtaposed with all graphs corresponding to the set of numbers m_k. It is clear that the configurational integral Z_n is equal to

$$Z_n = \sum_{(m_k)} S(m_k), \tag{65.11}$$

where the sum is taken over all sets of numbers m_k satisfying the condition expressed by formula (65.10).

The expression for the sum $S(m_k)$ can be obtained in the following way: we fix some definite labeling of the circles and divide n circles into k-groups with preset values of numbers m_k of k-groups. Further, we replace each of the k-groups by the sum of various possible k-groups. According to the definition, the group integral b_k, corresponding

to this k-particle graph is equal to

$$k!\, V\lambda^{3k-3}b_k.$$

And the integral corresponding to the entire n-particle graph is evidently equal to

$$\prod_{k=1}^{n} [k!\, V\lambda^{3k-3}b_k]\, m_k.$$

In order to obtain $S(m_k)$, we must now make all kinds of permutations of the circle labels 1, 2, . . ., n (of the variables $r_1, \ldots, r_n$), leading to new essentially different graphs. Since the values of integrals are independent of the notation of integration variables, all the obtained terms are the same, and to obtain $S(m_k)$, it is sufficient to multiply the previously obtained expression by the number of essentially different graphs. In this case by essentially different graphs are meant such that differ from one another in the set of variables $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$, present at least in two k-groups.

The finding of the number of such graphs is a combinatorial problem, dealt with above in the book.

Let us denote by W the number of essentially different graphs that is of interest to us. In each such graph we can carry out $k!$ permutations of the labels within each k-group and $m_k!$ permutations of k-groups between themselves. Neither of the permutations lead to new essentially different graphs. The total number of the thus obtained graphs

$$W \prod_k (k!)^{m_k} \prod_k (m_k)!$$

is equal, evidently, to $n!$, since the first factor accounts for the permutations of the labels among the k-groups, the second the permutations within the k-groups and the third the permutations of k-groups with each other, and an account is taken in this way of all the permutations of numbers.

Thus we have

$$W = \frac{n!}{\prod_{k=1}^{n} (k!)^{m_k}\, m_k!} \tag{65.12}$$

and, consequently, for $S(m_k)$ we obtain the expression

$$S(m_k) = n! \prod_{k=1}^{n} \frac{(V\lambda^{3k-3}b_k)^{m_k}}{m_k!} = n!\, \lambda^{3n} \prod_{k=1}^{n} \frac{1}{m_k!} \left(\frac{Vb_k}{\lambda^3}\right)^{m_k}, \tag{65.13}$$

where use was made of condition (65.10).

According to (65.11), the configurational integral Z_n is expressed by

$$Z_n = \sum_{(m_k)} S(m_k) = n! \lambda^{3n} \sum_{(m_k)} \prod_{k=1}^{n} \frac{1}{m_k!} \left(\frac{V b_k}{\lambda^3} \right)^{m_k}. \quad (65.14)$$

The transition from Z to the Q-sum by formula (65.4) permits elimination of condition (65.10):

$$Q(z, V, T) = \sum_{m_k=0}^{\infty} \prod_{k=1}^{\infty} \frac{1}{m_k!} \left(\frac{V z^k b_k}{\lambda^3} \right)^{m_k} = \exp\left(\frac{V}{\lambda^3} \sum_{k=1}^{\infty} b_k z^k \right), \quad (65.15)$$

whence we obtain for the Ω-potential the expression

$$\frac{\Omega}{T} = -\ln Q = -\frac{V}{\lambda^3} \sum_{k=1}^{\infty} b_k z^k. \quad (65.16)$$

The pressure and the number of particles are found to be expressed by

$$P = -\frac{\Omega}{V} = \frac{T}{\lambda^3} \sum_{k=1}^{\infty} b_k z^k,$$
$$N = -\frac{\partial \Omega}{\partial \mu} = -\frac{\partial \Omega}{\partial z} \frac{dz}{d\mu} = -\frac{z}{T} \frac{\partial \Omega}{\partial z}, \quad (65.17)$$

whence

$$N = \frac{V}{\lambda^3} \sum_{k=1}^{\infty} k b_k z^k. \quad (65.18)$$

In order to obtain the equation of state, activity z must be eliminated from formulae (65.17) and (65.18).

Lee and Yang have shown [16] that in the case of rarefied gases it is possible to pass in Eqs. (65.17) and (65.18) to the thermodynamic limit $V \to \infty$, $N \to \infty$ on the condition that $\omega = V/N$ remains finite, and replace the group integrals $b_k(V, T)$ by their limit values $\beta_k(T)$:

$$\beta_k(T) = \lim_{V \to \infty} b_k(V, T).$$

Then, we obtain

$$P = \frac{T}{\lambda^3} \sum_{k=1}^{\infty} \beta_k z^k, \quad (65.19)$$

$$\frac{1}{\omega} = \frac{1}{\lambda^3} \sum_{k=1}^{\infty} k \beta_k z^k. \quad (65.20)$$

Let us find the equation of state in the form of the so-called *virial expansion*

$$\frac{P\omega}{T}=\sum_{i=1}^{\infty}a_i(T)\left(\frac{\lambda^3}{\omega}\right)^{i-1}, \tag{65.21}$$

where the quantities $a_1(T)$, $a_2(T)$, . . . are called the first, the second, etc. *virial coefficients.*

Substituting into the left- and right-hand sides of expansion (65.21) expressions (65.20) and (65.19), we obtain

$$\frac{\sum\limits_{k=1}^{\infty}\beta_k z^k}{\sum\limits_{k=1}^{\infty}k\beta_k z^k}=\sum_{i=1}^{\infty}a_i(T)\Big[\sum_{k=1}^{\infty}k\beta_k z^k\Big]^{i-1},$$

or in an expanded form

$$(\beta_1 z+2\beta_2 z^2+3\beta_3 z^3+\ldots)\Big[a_1+a_2\sum_{k=1}^{\infty}k\beta_k z^k+a_3\Big(\sum_{k=1}^{\infty}k\beta_k z^k\Big)^2+\ldots\Big]$$
$$=\beta_1 z+\beta_2 z^2+\beta_3 z^3+\ldots. \tag{65.22}$$

This relationship must be satisfied identically for any z. Equating the coefficients at equal powers of z, we obtain

$$a_1(T)=\beta_1=1,\quad a_2(T)=-\beta_2,\quad a_3(T)=4\beta_2^2-2\beta_3, \tag{65.23}$$

and, consequently, all virial coefficients can be expressed in terms of the limit values of the group integrals at $V\to\infty$.

Let us approximately calculate $a_2(T)=-\beta_2$, using the information on the interaction energy $\mathcal{U}(r)$, outlined in the beginning of this section. We have

$$\beta_2=\frac{1}{2\lambda^3}\int d^3r f_{12}(r)$$
$$=\frac{2\pi}{\lambda^3}\Big\{\int_0^{r_0}[e^{-\mathcal{U}(r)/T}-1]\,r^2\,dr+\int_{r_0}^{\infty}[e^{-\mathcal{U}(r)/T}-1]\,r^2\,dr\Big\}.$$

Assuming the molecule to be a hard sphere with a radius equal to $r_0/2$, let us replace in the first integral $\mathcal{U}(r)$ by ∞; expanding in the second integral the exponential $e^{-\mathcal{U}(r)/T}\approx 1-\frac{|\mathcal{U}(r)|}{T}$, we obtain $\beta_2=\frac{1}{\lambda^3}\left(\frac{a}{T}-b\right)$, where $b=4\frac{4\pi}{3}\left(\frac{r_0}{2}\right)^3$ is the fourfold atomic volume, and the quantity

$$a=\frac{1}{2}4\pi\int_{r_0}^{\infty}|\mathcal{U}(r)|\,r^2\,dr$$

is associated with the mean potential energy due to molecular attractive forces.

Thus, accounting only for double collisions, we have

$$P=\frac{NT}{V}\left(1+\frac{Nb}{V}-\frac{aN}{TV}\right),$$

or

$$P+\frac{aN^2}{V^2}=\frac{NT}{V}\left(1+\frac{Nb}{V}\right).$$

We can obtain an interpolation formula, describing approximately not only the properties of a gas, but also of a fluid, by a substitution

$$1+\frac{Nb}{V}\approx\left(1-\frac{Nb}{V}\right)^{-1}.$$

Such a substitution roughly accounts for poor compressibility of liquids at $P\to\infty$, $V\to Nb$. The equation thus obtained,

$$\left(P+\frac{aN^2}{V^2}\right)(V-Nb)=NT$$

is the well-known van der Waals equation (see Sec. 12).

A complete calculation of the virial coefficients, determining the equation of state (65.21), is a very complicated problem that has not been fully solved so far.

Problems

1. N particles of a gas are confined within volume V, subdivided into cells of volume v. It is assumed that each cell can contain not more than one molecule, and the molecules occupying different cells are not interacting with one another—a model of a lattice gas. Calculate in the thermodynamic limit the virial coefficients a_i.

Answer. $a_i=\frac{1}{i}\left(\frac{v}{\lambda^3}\right)^{i-1}$.

2. Added to the conditions of problem 1 are the attractive forces acting between each pair of molecules, the potential of which is constant and equal to $-2a/V$ (a = const). Find the equation of state in the thermodynamic limit and the critical parameters.

Answer. $P=-\frac{T}{v}\ln\left(1-\frac{Nv}{V}\right)-\frac{aN^2}{V^2}$,

$$V_{cr}=2Nv,\quad P_{cr}=\frac{a}{2v^2}\left(\ln 2-\frac{1}{2}\right),\quad T_{cr}=\frac{a}{2v}.$$

66. Plasma. Debye's Screening

The method of calculation of thermodynamic functions for non-ideal gases considered in Sec. 65 is invalid for plasma—a gas characterized by the Coulomb interaction between particles, since, due to the long-range nature of the Coulomb forces, the Mayer functions, expressed by formula (65.5), $f_{ik} = \exp\left(\frac{\beta q_i q_k}{r_{ik}}\right) - 1$, is inversely proportional only to r_{ik} at large values of r_{ik}, and their integrals are divergent.

Physically, however, the fields of individual ions in plasma are screened, owing to the tendency of oppositely-charged particles to accumulate around ions of one sign.

Let plasma consist of ions of m kinds and electrons carrying a charge e_α, with a mean number of ions per unit volume equal to $n_\alpha^{(0)}$. Plasma is electrically neutral as a whole, so that

$$\sum_\alpha n_\alpha^{(0)} e_\alpha = 0. \tag{66.1}$$

We shall limit ourselves to the consideration of weakly non-ideal plasma in which the energy of the Coulomb interaction, $e_\alpha e_\beta / r_{\alpha\beta} \sim e^2 n^{1/3}$ ($n^{1/3}$ is the mean particle spacing), is small compared to the mean kinetic energy

$$n \ll \left(\frac{T}{e^2}\right)^3. \tag{66.2}$$

Plasma satisfying the above condition is referred to as *hot low-density plasma*.

Let us consider a field in the neighbourhood of an ion with a charge e_β (for the sake of simplicity we assume the ion to be located at the origin of coordinates). At $r \neq 0$ the electrostatic potential of the field satisfies the Poisson equation

$$\nabla^2 \varphi_\beta = -4\pi \sum_\alpha e_\alpha n_\alpha, \tag{66.3}$$

where, according to Boltzmann's distribution, the densities n are equal to

$$n_\alpha = n_\alpha^{(0)} e^{-e_\alpha \varphi_\beta / T}. \tag{66.4}$$

Due to the inequality (66.2) we can expand the exponential in formula (66.4) into a series in powers of $e_\alpha \varphi_\beta / T$ and limit ourselves to the first two terms of the expansion. Then, by condition (66.1), the sum on the right-hand side of formula (63.3) is presented by

$$\sum_\alpha e_\alpha n_\alpha = \sum_\alpha e_\alpha n_\alpha^{(0)} - \sum_\alpha e_\alpha^2 n_\alpha^{(0)} \frac{\varphi_\beta}{T} = -\frac{\varphi_\beta}{T} \sum_\alpha n_\alpha^{(0)} e_\alpha^2,$$

and equation (66.3) reduces to

$$\nabla^2\varphi_\beta = \varkappa^2\varphi_\beta,$$

where

$$\varkappa^2 = \frac{4\pi \sum_\alpha n_\alpha^{(0)} e_\alpha^2}{T}.$$

The spherically symmetric solution of this equation, decreasing as $r \to \infty$, is

$$\varphi_\beta = C_\beta \frac{e^{-\varkappa r}}{r},$$

which at $r \to 0$ turns into the unscreened Coulomb field of ion β. It follows from this that $C_\beta = e_\beta$ and

$$\varphi_\beta = e_\beta \frac{e^{-\varkappa r}}{r}, \tag{66.5}$$

At large r the potential expressed by formula (66.5) decreases exponentially in the main, and the quantity $\varkappa^{-1}$ determines the size of the neutralizing ion cloud. It is referred to as *Debye's radius**

$$\varkappa^{-1} = r_D = \left[\frac{T}{4\pi \sum_\alpha n_\alpha^{(0)} e^2}\right]^{1/2}. \tag{66.6}$$

The order of magnitude of the Debye radius is $\left(\frac{T}{ne^2}\right)^{1/2}$, and the inequality (66.2) can be rewritten in the form $r_D \gg n^{-1/3}$. Thus, when the Debye approximation is valid, Debye's radius is very large compared to the mean particle spacings, and a great number of particles is confined within Debye's sphere (see the problem to this section).

Let us find the correction to the internal energy of plasma due to Debye's screening. The energy of a system of charges is expressed by

$$\mathcal{U} = \frac{1}{2} V \sum_\alpha e_\alpha n_\alpha^{(0)} \tilde{\varphi}_\alpha, \tag{66.7}$$

where $\tilde{\varphi}_\alpha$ is the potential of the field acting upon the ion e_α from the side of the remaining ions. Expanding the exponential in formula (66.5) into a power series in r, we obtain

$$\varphi_\alpha = \frac{e_\alpha}{r} - e_\alpha\varkappa + \frac{1}{2} e_\alpha \varkappa^2 r + \ldots . \tag{66.8}$$

At $r \to 0$ the first term of the expansion represents the Coulomb field of the ion proper e_α, the second term, the potential of other ions of the "cloud" at the point where the ion e_α is located, i.e. $\tilde{\varphi}_\alpha$, and the

* Debye and Hückel applied this technique in studying electrolytes.

contribution of the remaining terms tends to zero together with r. In this way, substituting into formula (66.7) $\tilde{\varphi}_\alpha = -e_\alpha \varkappa$ and using formula (66.6), we obtain

$$\mathcal{U} = -\left(\frac{\pi}{TV}\right)^{1/2} \left(\sum_\alpha N_\alpha e_\alpha^2\right)^{3/2}, \tag{66.9}$$

where $N_\alpha = n_\alpha^{(0)} V$ is the total number of ions of the α kind. Formula (66.9) was used in Sec. 20 in studying the phenomenological theory of plasma.

Problem

Plasma contains two kinds of particles: electrons and ions with the charge Ze. In a hot low-density electrically neutral plasma approximation find: (1) the Debye radius; (2) electron and ion density in the "cloud" surrounding the ion n_e, n_i; (3) the number of excessive (compared to the mean) electrons and ions ΔN_e, ΔN_i and the excessive charges ΔQ_e and ΔQ_i in the "cloud"; (4) the mean number of electrons and ions in the "cloud", N_e and N_i.

Answer. (1) $r_D = \left[\frac{T}{4\pi n_e^{(0)} e^2 (Z+1)}\right]^{1/2}$;

(2) $n_e = n_e^{(0)} \left(1 + \frac{e\varphi_i}{T}\right) = n_e^{(0)} \left(1 + \frac{Ze^2}{T} e^{-r/r_D}\right)$,

$n_i = \frac{n_e^{(0)}}{Z} \left(1 - \frac{Z^2 e^2}{T} e^{-r/r_D}\right)$;

(3) $\Delta N_e = \frac{Z}{Z+1}$, $\Delta N_i = -\frac{Z}{Z+1}$;

$\Delta Q_e = -\frac{Ze}{Z+1}$, $\Delta Q_i = -\frac{Z^2 e}{Z+1}$;

(4) $N_e = \frac{1}{6\sqrt{\pi}} \left[\frac{T}{(n_e^{(0)})^{1/3} e^2 (Z+1)}\right]^{3/2} \gg 1$,

$N_i = \frac{1}{6\sqrt{\pi} Z} \left[\frac{T}{(n_e^{(0)})^{1/3} e^2 (Z+1)}\right]^{3/2} \gg 1$.

67*. Extreme and Negative Temperatures

Most of the physical systems dealt with in statistical physics, referred to below as *normal systems*, possess the following two properties: firstly, they have an unlimited from above energy spectrum (if only because the magnitude of the kinetic energy is not limited, and any system consists of moving particles); secondly, the density of states with a given energy $g(E_i)$ rises with increasing energy, obeying a power law. For an ideal gas, for instance (Sec. 61), $g(E) = \frac{d\Gamma}{dE} \propto E^{3N/2}$.

In such systems temperature must be positive and assume any value within the interval $0 \leqslant T < \infty$. Indeed, for the series expressing the partition function $Z = \sum_i g(E_i) e^{E_i/T}$ to converge, firstly, the inequality $T \geqslant 0$ must be valid and, secondly, if this condition is satisfied, any positive temperatures are admissible, since the increase of the function $g(E)$ by a power law at any $T > 0$ is more than compensated for by the exponential decrease of the factor $e^{-E_i/T}$.

"Special" physical system can, however, be visualized for which at least one of the criteria of the system normality is violated. Let us consider several possible "*anomalous*" *systems* [17].

1. Let $g(E_i)$ increase at large energies, obeying not a power, but an exponential law: $g(E_i) \propto e^{aE_i}$ $(a > 0)$. In this case the common term of the series in the expression for Z behaves at large values of E_i as $\exp\left[\left(a - \frac{1}{T}\right) E_i\right]$, and for the convergence of this series the condition $0 \leqslant T < 1/a$ should be satisfied. Thus the temperature is positive, but there exists an extreme temperature $T_{ex} = \frac{1}{a}$, above which the system cannot be heated.

2. Consider now a system in which the density of states $g(E_i)$ does not increase but diminishes with increasing energy. If the density of states $g(E_i)$ decreases following a power law, the properties of this system can readily be seen to coincide with the properties of a normal system, and the temperature variation interval is $0 \leqslant T < \infty$ as before.

If at high values of E_i, $g(E_i)$ decreases exponentially, $g(E_i) \propto e^{-aE_i}$, then the common term of the series for the partition function Z behaves at large values of E_i as $\exp[-(a + 1/T)E_i]$. Then, the condition of convergence of the series requires the fulfilment of the inequality

$$a + \frac{1}{T} = \frac{Ta + 1}{T} \geqslant 0.$$

It follows from here that either $T \geqslant 0$ or $T < -1/a$, i.e. for such a system the temperature can be both positive $0 \leqslant T < \infty$ and negative, and in the latter case there exists an extreme negative temperature $T_{ex} = -1/a$ above which the system cannot be heated, $-\infty < T < T_{ex}$.

3. A system can be visualized in which the energy spectrum is limited from above and there exists a maximum energy E_{max}. Such a system can be considered as a limiting case of system 2, when the parameter a becomes infinity, and $g(E_i)$ becomes zero beginning with $E_i = E_{max}$. This case will be shown to be of the greatest practical interest. The series representing Z turns then into a finite sum and Z has a finite value at any T, both positive and negative, and the temperature variation interval is $-\infty < T < \infty$.

To elucidate the physical meaning of the extreme and negative temperatures, let us see how the partition function Z, the probability of the value of energy E_i and the mean energy $\bar{E}$, specified respectively by formulae (63.13) through (63.15), change with temperature:

$$Z = \sum_i g(E_i)\, e^{-E_i/T}, \quad W(E_i) = \frac{1}{Z}\, g(E_i)\, e^{-E_i/T},$$

$$\bar{E} = \frac{1}{Z} \sum_i E_i g(E_i)\, e^{-E_i/T}, \tag{67.1}$$

both for normal systems and for systems 1-3.

Normal system. In this case, at $T \to 0$ we have

$$Z \to g(0), \quad W(E_i) = \delta_{i,1}, \quad \bar{E} \to 0,$$

since as $T \to +0$ all the exponentials $e^{-E_i/T} \to 0$ except the exponential with $E_i = E_1 = 0$, which is equal to unity. This means that as $T \to 0$ the system has zero energy for certain. At $T > 0$ the exponentials $e^{-E_i/T}$ are decreasing, i.e. the probability of higher values

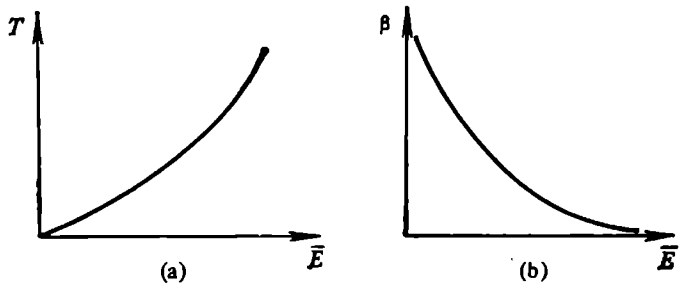


FIG. 86

of energy is less than the probability of lower values. Finally, as $T \to \infty$, $e^{-E_i/T} \to 0$, i.e. all states of the system become equiprobable and the series in the expression for the partition function becomes divergent. As $T \to \infty$ we have

$$Z \to \sum_i g(E_i) = \infty, \quad W(E_i) \to \frac{g(E_i)}{\sum_i g(E_i)}, \quad \bar{E} \to \frac{\sum_i E_i g(E_i)}{\sum_i g(E_i)} = \infty,$$

since the series in the numerator diverges at a higher rate than the series in the denominator. Figure 86 shows the mean energy as a function of temperature (Fig. 86 (*a*)) and the behaviour of the temperature variable $\beta = 1/T$ (Fig. 86 (*b*)).

Case 1. Let us assume for the sake of simplicity that all energies are expressed by the formula $g(E_i) = e^{aE_i}$. Then, according to formula (67.1), as $T \to 0$ the same situation arises as in the case of a normal system, i.e.

$$e^{(a-1/T)E_i} \to \delta_{i,1}$$

and, consequently,

$$Z \to 1, \quad W(E_i) \to \delta_{i,1}, \quad \bar{E} \to 0.$$

The system has zero energy for certain.

At $T > 0$ the probability of different states drops with rising E_i, but in contrast to normal systems, the equiprobability of all states

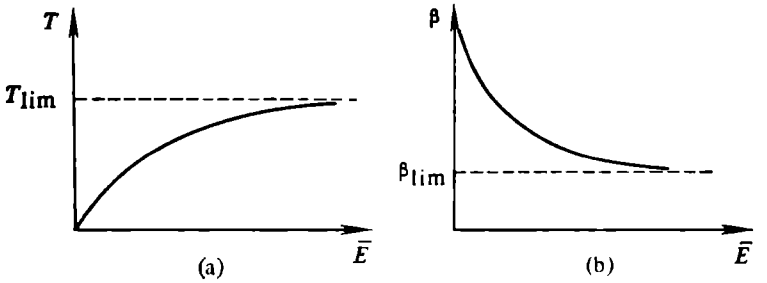


FIG. 87

is attained already at $T \to T_{ex} = 1/a$; in this case all the exponentials $e^{(a-1/T)E_i} \to 1$ and the partition function becomes divergent at $T = T_{ex}$:

$$Z \to \sum_i 1, \quad W(E_i) \to \frac{1}{\sum_i 1}, \quad \bar{E} \to \frac{\sum_i E_i}{\sum_i 1} = \infty.$$

The dependences $T(\bar{E})$ and $\beta(\bar{E})$ are shown in Fig. 87.

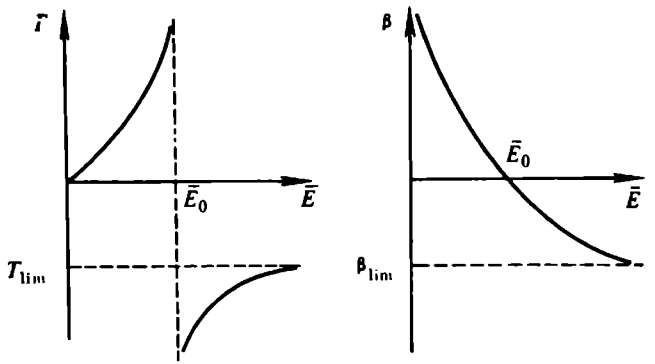
Case 2. We have $g(E_i) = e^{-aE_i}$; then it follows from formula (67.1) that as $T \to +0$, as before, $\exp\left[-\left(a + \frac{1}{T}\right) E_i\right] \to \delta_{i,1}$ and consequently the system has zero energy:

$$Z \to 1, \quad W(E_i) = \delta_{i,1}, \quad \bar{E} = 0.$$

At $T > 0$ high values of energy are less probable than low ones. As $T \to \infty$ we obtain

$$Z = \sum_i e^{-aE_i}, \quad W(E_i) \to \frac{e^{-aE_i}}{\sum_i e^{-aE_i}}, \quad \bar{E} \to \frac{\sum_i E_i e^{-aE_i}}{\sum_i e^{-aE_i}} = E_0.$$

All the above expressions are seen to be finite and the probabilities of all microstates become equal: $W(E_l) \propto e^{-aE_l} \propto g(E_l)$. The formula for $\bar{E}$ shows that in this extreme case the energy $\bar{E}$ is equal to the mean arithmetic energy E_0. This situation also remains in the case when the system temperature undergoes a discontinuity jump



(a) (b)

FIG. 88

and becomes equal to $-\infty$. At $T < 0$ an inversion of probabilities occurs—the probability of the system having an energy E_l does not decrease but increases with rising E_l, and $\bar{E}$ becomes higher than E_0. Finally, at $T \to T_{ex} = -1/a$ we obtain

$$Z \to \sum_i 1, \quad W(E_l) \to \frac{1}{\sum_i 1}, \quad \bar{E} \to \frac{\sum_l E_l}{\sum_i 1} = \infty.$$

The dependences $T(\bar{E})$ and $\beta(\bar{E})$ are depicted in Fig. 88.

Case 3. Repeating the same reasonings as in the preceding cases, we find that:

as $T \to +0$

$$Z \to g(0), \quad W(E_l) \to \delta_{l,1}, \quad \bar{E} = 0,$$

as $T \to \pm\infty$

$$Z \to \sum_i g(E_l), \quad W(E_l) \to \frac{g(E_l)}{\sum_l g(E_l)}, \quad \bar{E} \to \frac{\sum_l E_l g(E_l)}{\sum_i g(E_l)} = E_0.$$

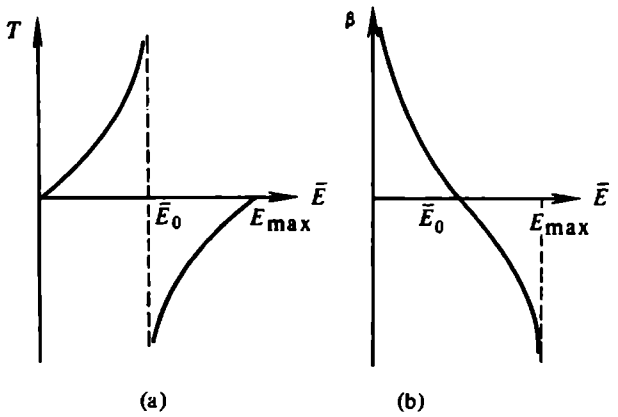
As $T \to -0$, the main contribution to the partition function is made by the term including $E_l = E_{max}$, while all other terms are

exponentially small compared to it; therefore, as $T \to -0$

$$Z = g(E_{\max}) e^{-E_{\max}/T}, \quad W(E_i) = \delta_{i, i_{\max}}, \quad \bar{E} = E_{\max}.$$

The system possesses a maximum possible energy for certain. The dependences $T(\bar{E})$ and $\beta(\bar{E})$ are plotted in Fig. 89.

The reader's attention should be drawn to the fact that for systems 2 and 3 (systems with negative temperatures) the variable $\beta = 1/T$ is by far more convenient and adequate (from the viewpoint



(a) (b)

FIG. 89

of phenomenological physics) measure of the mean energy than temperature. As the mean energy increases from zero to infinity in case 2, or from zero to $E_{\max}$ in case 3, the variable β decreases continuously from ∞ to $\beta_{ex} = 1/T_{ex}$ in case 2, or to $-\infty$ in case 3, whereas temperature T rises from 0 to ∞, then undergoes a discontinuity jump $-\infty$ and rises again to T_{ex} in case 2, or to zero in case 3.

It follows from cases 2 and 3 considered above that the negative temperatures are "higher" than the positive ones, and the mean energy of the system with $T < 0$ is higher than at any temperature $T > 0$.

Let us turn to the physical realization of systems with extreme and negative temperatures. At present no practical systems with extreme temperatures are known. Some formal model, possessing a positive extreme temperature, can, however, be pointed out. Let an ideal gas, consisting of N particles with mass m, be confined between two planes $z = 0$ and $z = H$ in an axisymmetric field with a potential

$$\mathcal{U}(r) = \begin{cases} 0 & \text{at } a \geqslant r, \\ 2\mathcal{U}_0 \ln(r/a) & \text{at } a < r, \end{cases}$$

where z, r, φ are cylindrical coordinates. It can readily be seen that at high values of E the function $\rho(E)$ increases obeying the exponential

law $e^{E/\mathcal{U}_0}$. In fact, for the number of states of one particle with energy lower than E we have

$$\Omega(E) = \int \frac{d\Gamma}{h^3} = \frac{8\pi^2 H}{h^3} \int_0^{\sqrt{2mE}} p^2\,dp \int_0^b r\,dr,$$

where $b = a \exp\left[\left(E - \frac{p^2}{2m}\right)/2\mathcal{U}_0\right]$. Integrating over r, with the integration limit in plane p, r being determined by the equation

$$\frac{p^2}{2m} + 2\mathcal{U}_0 \ln \frac{r}{a} = \bar{E},$$

we obtain

$$\Omega(E) = \frac{4\pi^2 H a^2}{h^3} e^{E/\mathcal{U}_0} \int_0^{\sqrt{2mE}} p^2 \exp\left[-\frac{p^2}{2m\mathcal{U}_0}\right] dp.$$

At large values of E the last integral tends to

$$\int_0^\infty p^2 \exp\left[-\frac{p^2}{2m\mathcal{U}_0}\right] dp = \frac{\sqrt{\pi}}{4} (2m\mathcal{U}_0)^{3/2}$$

and

$$g(E) \propto \frac{d\Omega}{dE} \propto e^{E/\mathcal{U}_0}.$$

In accordance with the above reasonings, the system must possess an extreme temperature $T_{ex} = \mathcal{U}_0$.

Let us consider now the possibility of realizing systems with an energy spectrum limited from above, i.e. systems with negative temperatures. It should be noted in the first place that states with negative temperatures can be very descriptively interpreted in the case of a system of weakly interacting particles, when it is possible to speak of energy levels of individual particles and about their "populations". The population of levels, i.e. the number of particles occupying a given level, is then proportional to the Maxwell-Boltzmann factor $e^{-\varepsilon_i/T}$, and at $T > 0$ the population of levels drops with increasing energy—the population of the upper levels is lower than that of the lower levels. As $T \to \infty$, $e^{-\varepsilon_i/T} \to 1$ and all the levels are uniformly populated. Finally, after temperature undergoes a discontinuity jump to $-\infty$ and rises again being already negative, the factor $e^{-\varepsilon_i/T}$ becomes an increasing function of ε_i, and the so-called *population inversion* takes place, consisting in the fact that on the upper energy levels there are more particles than on the lower ones.

It should be emphasized that the physical reason for the appearance of the extreme and negative temperatures consists in the following.

The population of the ith level is proportional to the product of two factors depending on energy: $g(\varepsilon_i)$ and $e^{-\varepsilon_i/T}$. If, beginning with a certain temperature T_{cr}, positive or negative, this product becomes an increasing function of ε_i (cases 1 and 2), then it is impossible to populate an infinite succession of levels with a finite number of particles N. This manifests itself mathematically in the divergence of the partition function Z. On the contrary, if $g(\varepsilon_i)$ decreases sufficiently rapidly with rising ε_i (cases 2 and 3), the finite number of particles is sufficient to populate all the levels, even at $T < 0$.

As was already mentioned at the beginning of this section, all the macroscopic systems dealt with in statistical physics have an energy spectrum not limited from above. Some system's degrees of freedom can have, however, limited energy spectra. For instance, let the particles forming a crystal lattice have spin s and the lattice be placed in a magnetic field of intensity H. The projection of the angular momentum on the magnetic field direction can have $2s + 1$ different values from $-\frac{sh}{2\pi}$ to $+\frac{sh}{2\pi}$, and for each value of the projection of the angular momentum there exists its proper value of the energy of the magnetic dipole in the magnetic field, $-\mu H$, where $\mu = \mu_B s/s$ is the magnetic moment of a particle. Thus, the energy spectrum of spin degrees of freedom is limited from below and from above. The energy assumes a minimum value when the magnetic moment is parallel to the field, and a maximum value when the magnetic moment is antiparallel to the field.

It is, therefore, possible to introduce the concept of negative temperatures. In the simplest case when $s = 1/2$, the temperature equal to $T = 0$ is associated with an ordered arrangement of magnetic moments parallel to the field (the magnetic spin number for all of the ions is $m_s = 1/2$), positive temperatures with a partly ordered arrangement (for most ions $m_s = 1/2$); a temperature equal to $\pm\infty$ corresponds to a random state (the number of ions with $m_s = 1/2$ and $m_s = -1/2$ is the same).

Negative temperatures are associated with a partly ordered state with a magnetic moment mostly directed antiparallel to the field (for most ions $m_s = -1/2$) and, finally, temperature $T = -0$ is associated with a completely ordered state and magnetic moments of particles directed antiparallel to the field (for all ions $m_s = -1/2$).

States with negative temperatures can be practically realized by reversing rapidly the direction of the magnetic field—the magnetic moments preliminarily oriented by that field preserve their previous orientation for some period of time.

It must be realized that for all real systems the states with negative temperatures are, strictly speaking, not equilibrium states but merely metastable states. In fact, the state of a spin system with magnetic moments oriented antiparallel to the field is unstable, since

it possesses excessive energy. In the characteristic time interval during which energy is transferred from the spin degrees of freedom to the rotational and vibrational degrees of freedom the state is destroyed and a state sets in in which the spins are mainly oriented parallel to the field. In terms of temperature it means that a system with negative temperature will cool and pass to a state with positive temperature, transferring the excess energy to other degrees of freedom.

As a consequence of this, we can speak of negative temperature only in some conditional sense in cases when the complete thermodynamic equilibrium time—the time of energy equipartition between all degrees of freedom—considerably exceeds the spin-spin relaxation time or the thermodynamic equilibrium time for the orientation of spin moments.

The concept of negative temperature has a still more conditional sense in the theory of quantum oscillators and amplifiers of electromagnetic waves (see Sec. 84).

Let us consider a physical problem in which only a limited number of atomic or molecular energy levels are of essential importance, usually two or three levels, and a population inversion is created with respect to these levels, i.e. more particles occupy the upper level than the lower one. Let this overpopulation of the upper levels be continuously maintained by "pumping" particles onto the upper level. Then, we can speak in a rather conditional sense of "negative" temperature with respect to these levels. It should be noted that, strictly speaking, the concept of temperature is the concept of thermodynamics of equilibrium processes, and is applicable to the processes considered above with the same reservations as, for instance, when considering a rod, one end of which is maintained at a higher temperature than the other end.

Problem

A Maxwell-Boltzmann gas is placed in a cylindrically symmetric magnetic field with a potential

$$\mathcal{U}(\rho) = \begin{cases} \infty \text{ at } \rho > a, \\ \mathcal{U}_0 \ln(\rho/a) \text{ at } \rho < a. \end{cases}$$

Show that there exists in this model a minimum low temperature below which the gas cannot be cooled. Explain the reason for this paradox.

68. Second Quantization

As is known from quantum mechanics, the state of a system consisting of identical particles is described by wave functions $\psi(q_1, q_2, \ldots, q_N)$ possessing symmetry properties in the case of a boson

system, or antisymmetry properties in the case of a fermion system, with respect to permutations of pairs of arguments q_i, q_k. Here q_i denotes the total set of arguments characterizing a particle; for instance, in a coordinate representation it is the set of space coordinates x_i, y_i, z_i and spin variable σ_i for particles with spin. In a momentum representation, instead of the coordinates x_i, y_i, z_i, we can choose as arguments of the wave function the momentum projections ξ_i, η_i, ζ_i, etc.

For a system of weakly interacting identical particles there is one more important representation—the occupation number, or the *second quantization representation*. For a system of weakly interacting particles single-particle wave functions $\varphi_k(q_i)$ can be introduced as an approximation. These functions describe the state of an individual particle in the absence of all other particles. It is convenient, though not necessary, to assume the single-particle wave functions $\varphi_k(q_i)$ to be the eigenfunctions of some Hermitian single-particle operator $\hat{L}$—the operator of particle energy, particle momentum, particle angular momentum, etc. This means that the functions φ_k satisfy the following equation:

$$\hat{L}\varphi_k(q) = L_k\varphi_k(q). \tag{68.1}$$

In this case the system of functions $\varphi_k(q)$ can always be assumed to be orthonormal:

$$\int \varphi_k^*(q)\,\varphi_l(q)\,dq = \delta_{kl}. \tag{68.2}$$

The symmetric and antisymmetric functions for this system can then be constructed from $\varphi_k(q)$ according to the following formulae:

$$\psi_s = \sum_P \varphi_{k_1}(q_1)\,\varphi_{k_2}(q_2)\ldots\varphi_{k_N}(q_N), \tag{68.3}$$

$$\psi_a = \sum_P \delta_P\varphi_{k_1}(q_1)\,\varphi_{k_2}(q_2)\ldots\varphi_{k_N}(q_N) = \begin{vmatrix} \varphi_{k_1}(q_1) & \varphi_{k_1}(q_2) & \ldots & \varphi_{k_1}(q_N) \\ \varphi_{k_2}(q_1) & \varphi_{k_2}(q_2) & \ldots & \varphi_{k_2}(q_N) \\ \ldots & \ldots & \ldots & \ldots \\ \varphi_{k_N}(q_1) & \varphi_{k_N}(q_2) & \ldots & \varphi_{k_N}(q_N) \end{vmatrix}. \tag{68.4}$$

Summation is carried out over all permutations of P indices k_1, k_2, . . ., k_N, and δ_P is equal to $+1$ for permutations consisting of an even number of paired permutations (transpositions) and -1 for permutations consisting of an odd number of transpositions.

By virtue of particle indistinguishability—symmetry or antisymmetry of functions (68.3), (68.4) respectively—these functions are defined unambiguously if it is indicated how many indices of single-

particle wave functions are equal to 1, how many of them are equal to 2, etc. This means that we can turn to the representation in which the arguments of the wave function are the occupation numbers n_1, n_2, . . ., indicating the number of particles in state 1, state 2, etc. It should be borne in mind that the above reasoning is valid only on the assumption of weak interaction, since in a system of strongly interacting particles we cannot speak of the states of individual particles.

In this representation the wave functions are written down in the form $\chi(n_1, n_2, \ldots)$. In this case, for a system of bosons the numbers n_i can take any integer values, $n_i = 0, 1, 2, \ldots$, and for a system of fermions only the values $n_i = 0, 1$.

Let us find the form of the most important operators in a second quantization representation.

Let us introduce the particle-number operator $\hat{N}$ whose eigenvalues coincide with the number of system's particles. It is also reasonable to introduce the operator $\hat{\rho}(\mathbf{r})$ of the particle density at the point r. The operators $\hat{N}$ and $\hat{\rho}(\mathbf{r})$ are obviously related as follows:

$$\hat{N} = \int \hat{\rho}(\mathbf{r})\, d^3r. \tag{68.5}$$

In quantum mechanics the probability density of finding the particle $\rho(\mathbf{r})$ is expressed in terms of the particle wave function by the formula $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2 = \psi^*(\mathbf{r})\,\psi(\mathbf{r})$. It is, therefore, permissible to introduce the operator wave function $\hat{\psi}(\mathbf{r})$ so as to ensure fulfilment of the relationship

$$\hat{\rho}(\mathbf{r}) = \hat{\psi}^+(\mathbf{r})\,\hat{\psi}(\mathbf{r}), \tag{68.6}$$

where $\hat{\psi}^+(\mathbf{r})$ is a Hermitian conjugate operator to the operator $\hat{\psi}(\mathbf{r})$.

The function $\hat{\psi}(\mathbf{r})$ introduced in this way is called the *secondly quantized wave function*. It should be noted that $\hat{N}$ and $\hat{\rho}(\mathbf{r})$ are Hermitian operators of physical quantities, whereas the operator wave function $\hat{\psi}(\mathbf{r})$ is not a Hermitian operator. Let us expand the operator $\hat{\psi}(\mathbf{r})$ into a series in an orthonormal system of single-particle wave functions:

$$\hat{\psi}(\mathbf{r}) = \sum_k \hat{a}_k \varphi_k(\mathbf{r}), \quad \hat{\psi}^+(\mathbf{r}) = \sum_k \hat{a}_k^+ \varphi_k^*(\mathbf{r}). \tag{68.7}$$

The coefficients $\hat{a}_k$, $\hat{a}_k^+$ are Hermitian conjugate operators with as yet unspecified properties.

It follows from formulae (68.7), (68.2) that the particle-number operator $\hat{N}$ is expressed by

$$\hat{N} = \sum_{i,k} \hat{a}_i^+ \hat{a}_k \int \varphi_i^*(\mathbf{r})\,\varphi_k(\mathbf{r})\, d^3r = \sum_k \hat{a}_k^+ \hat{a}_k. \tag{68.8}$$

It is clear from formula (68.8) that the operators $\hat{n}_k = \hat{a}_k^+ \hat{a}_k$ have the meaning of the particle-number operators in the kth state. The relationship $\hat{a}_k^+ \hat{a}_k = \hat{n}_k$ reminds one somewhat of the expansion of a wave function $\psi(\mathbf{r})$ in an arbitrary orthonormal basis $\varphi_k(\mathbf{r})$, where the squared modules are the probabilities of finding the system in the states $\varphi_k(\mathbf{r})$.

We shall construct an arbitrary wave function of the system $\chi(n_1, n_2, \ldots)$, depending on the occupation numbers, as a superposition of the products of the operator's eigenfunctions:

$$\hat{n}_k \chi_{n_k'}(n_k) = n_k' \chi_{n_k'}(n_k), \tag{68.9}$$

$$\chi(n_1, n_2, \ldots) = \sum_{n_1', n_2', \ldots} c(n_1', n_2', \ldots) \chi_{n_1'}(n_1) \chi_{n_2'}(n_2) \ldots . \tag{68.10}$$

The eigenvalues of operators $\hat{n}_k$ depend essentially on the properties of the particles of the system under consideration. As has already been mentioned, if these particles are bosons, then the operators $\hat{a}_k$ must be so constructed that the numbers n_k' can take the values 0, 1, 2, ... For a system of fermions n_k' must take only two values, 0 or 1. It will be shown below that to satisfy these requirements it is sufficient to impose on the operators the following commutation relations.

1. A system of Bose particles.

$$\hat{a}_i \hat{a}_k - \hat{a}_k \hat{a}_i = 0, \quad \hat{a}_i^+ \hat{a}_k^+ - \hat{a}_k^+ \hat{a}_i^+ = 0, \quad \hat{a}_i \hat{a}_k^+ - \hat{a}_k^+ \hat{a}_i = \delta_{ik}. \tag{68.11}$$

2. A system of Fermi particles.

$$\hat{a}_i \hat{a}_k + \hat{a}_k \hat{a}_i = 0, \quad \hat{a}_i^+ \hat{a}_k^+ + \hat{a}_k^+ \hat{a}_i^+ = 0, \quad \hat{a}_i \hat{a}_k^+ + \hat{a}_k^+ \hat{a}_i = \delta_{ik}. \tag{68.12}$$

Let us consider the two cases separately.

Bose systems. Let $\chi_{n_k'}(n_k)$, n_k' be respectively the eigenfunction and eigenvalue of operation $\hat{n}_k = \hat{a}_k^+ \hat{a}_k$. Then

$$\hat{n}_k \chi_{n_k'}(n_k) = \hat{a}_k^+ \hat{a}_k \chi_{n_k'}(n_k) = n_k' \chi_{n_k'}(n_k).$$

Applying the operator $\hat{a}_k$ to both sides of the above equation and using the commutation relation (68.11), we obtain

$$\hat{a}_k \hat{a}_k^+ \hat{a}_k \chi_{n_k'}(n_k) = (\hat{a}_k^+ \hat{a}_k + 1)\, \hat{a}_k \chi_{n_k'}(n_k) = n_k' \hat{a}_k \chi_{n_k'}(n_k),$$

or

$$\hat{n}_k \{\hat{a}_k \chi_{n_k'}(n_k)\} = (n_k' - 1) \{\hat{a}_k \chi_{n_k'}(n_k)\}. \tag{68.13}$$

Thus, we have proven **lemma 1**: if n_k' and $\chi_{n_k'}(n_k)$ are the eigenvalue and the eigenfunction of operator n_k, then $\hat{a}_k \chi_{n_k'}(n_k)$ is also the

eigenfunction of operator $\hat{n}_k$, belonging to the eigenvalue $n'_k - 1$. This permits the operator $\hat{n}_k$ to be referred to as the particle annihilation operator in the kth state.

Multiplying formula (68.9) by $\hat{a}_k^+$, we get

$$\hat{a}_k^+ \hat{a}_k^+ \hat{a}_k \chi_{n'_k}(n_k) = n'_k \hat{a}_k^+ \chi_{n'_k}(n_k),$$

or

$$\hat{a}_k^+ (\hat{a}_k \hat{a}_k^+ - 1)\, \chi_{n'_k}(n_k) = n'_k \hat{a}_k^+ \chi_{n'_k}(n_k),$$

and, finally,

$$\hat{n}_k \{\hat{a}_k^+ \chi_{n'_k}(n_k)\} = (n'_k + 1)\{\hat{a}_k^+ \chi_{n'_k}(n_k)\}. \tag{68.14}$$

Thus, we have proven **lemma 2**: if n'_k and $\chi_{n'_k}(n_k)$ are the eigenvalue and the eigenfunction of operator $\hat{n}_k$, then $\hat{a}_k^+ \chi_{n'_k}(n_k)$ is also an eigenfunction of operator $\hat{n}_k$, belonging to the eigenvalue $n'_k + 1$. This permits the operator $\hat{a}_k^+$ to be referred to as the particle creation operator in the kth state.

It is clear that if n'_k is the eigenvalue of operator $\hat{n}_k$, then there exists a sequence of eigenvalues and eigenfunctions

$$n'_k,\ n'_k - 1,\ \ldots,\ n'_k - l;\quad \chi_{n'_k}(n_k),$$
$$\hat{a}_k \chi_{n'_k}(n_k),\ \ldots,\ (\hat{a}_k)^l \chi_{n'_k}(n_k).$$

Since there can be no negative eigenvalues for $\hat{n}_k$, this sequence must end, i.e. there must exist a minimum eigenvalue $n_k^{(0)}$ for which the equality $\hat{a}_k \chi_{n_k^{(0)}} = 0$ holds true. If $\hat{a}_k \chi_{n_k^{(0)}} \neq 0$, there would then exist an eigenvalue $n_k^{(0)} - 1$, which is impossible due to the existence of the minimum eigenvalue $n_k^{(0)}$.

Since $\hat{a}_k^+ \hat{a}_k \chi_{n_k^{(0)}} = 0$, we draw the conclusion that the minimum eigenvalue of operator $\hat{n}_k$ is $n_k^{(0)} = 0$, and that the sequence of eigenvalues of operator $\hat{n}_k$ is a sequence of non-negative integers 0, 1, 2, . . ., belonging to the sequence of functions $\chi_0(n_k)$, $\chi_1(n_k) \propto \hat{a}_k^+ \chi_0(n_k)$, ...

Let us select a representation in which the operator $\hat{n}_k$ is diagonal and the eigenvalues are arranged on the main diagonal in increasing order:

$$\hat{n}_k = \begin{vmatrix} 0 & 0 & 0 & \ldots & 0 & \ldots \\ 0 & 1 & 0 & \ldots & 0 & \ldots \\ 0 & 0 & 2 & \ldots & 0 & \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \ldots & l & \ldots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \tag{68.15}$$

It is clear that the orthonormal eigenfunctions of this operator are the columns

$$\chi_{n_k'}(n_k) = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \tag{68.16}$$

in which unity stands in the row numbered n_k' and the zeros are arranged in the other rows. The following equality is valid:

$$\hat{n}_k \chi_{n_k'}(n_k) = n_k' \chi_{n_k'}(n_k). \tag{68.17}$$

The conjugate function is defined as the row

$$\chi^+_{n_k'}(n_k) = (0, 0, \ldots, 0, 1, 0, \ldots), \tag{68.18}$$

in which unity stands in the column numbered n_k', and the other places are occupied by zeros. It satisfies the equation

$$\chi^+_{n_k'}(n_k)\, \hat{n}_k = n_k' \chi^+_{n_k'}(n_k). \tag{68.19}$$

Thus, in the columns $\chi_{n_k'}(n_k)$ the second quantizaton operators act on the left, and in the rows $\chi^+_{n_k'}(n_k)$ on the right.

The scalar product of a row and column is determined by ordinary multiplication, and we obtain

$$\chi^+_{n_k'}(n_k)\, \chi_{n_k''}(n_k) = \delta_{n_k' n_k''}. \tag{68.20}$$

The common eigenfunctions $\chi_{n_1', n_2', \ldots}(n_1, n_2, \ldots)$ of all operators $\hat{n}_k$ $(k = 1, 2, \ldots)$ are, evidently, the product

$$\chi_{n_1', n_2', \ldots}(n_1, n_2, \ldots) = \prod_k \chi_{n_k'}(n_k). \tag{68.21}$$

Let us find in this representation the form of the operators $\hat{a}_k$ and $\hat{a}_k^+$. According to lemmas 1 and 2, we have

$$\hat{a}_k^+ \chi_{n_k'}(n_k) = \alpha_{n_k'} \chi_{n_k'+1}(n_k), \quad \hat{a}_k \chi_{n_k'}(n_k) = \beta_{n_k'} \chi_{n_k'-1}(n_k),$$

whence, finding the matrix elements of the left-hand and right-hand sides, we obtain

$$(\hat{a}_k^+)_{n_k'', n_k'} = \alpha_{n_k'} \delta_{n_k'', n_k'+1}, \quad (\hat{a}_k)_{n_k'', n_k'} = \beta_{n_k'} \delta_{n_k'', n_k'-1}. \tag{68.22}$$

To find $\alpha_{n_k'}$, $\beta_{n_k'}$, we make use of the fact that $\hat{a}_k^+$ and $\hat{a}_k$ are Hermitian conjugates, leading to the equation

$$\alpha_{n_k'} = \beta^*_{n_k'+1},$$

and the relationship $\hat{n}_k = \hat{a}_k^+ \hat{a}_k$, which yields

$$\alpha_{n_k'} \beta_{n_k'+1} = n_k' + 1.$$

Accurate within the insignificant phase factor $e^{i\gamma(n_k')}$, we find from the above that

$$\alpha_{n_k'} = \beta^*_{n_k'+1} = \sqrt{n_k' + 1}, \tag{68.23}$$

and that the matrices $\hat{a}_k$ and $\hat{a}_k^+$ have the following form:

$$\hat{a}_k = \begin{vmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix}, \quad \hat{a}_k^+ = \begin{vmatrix} 0 & 0 & 0 & \dots \\ \sqrt{1} & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & \sqrt{3} & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}. \tag{68.24}$$

It will be readily seen that the application of operators $\hat{a}_k^+$ and $\hat{a}_k$ to the function $\chi_{n_k'}(n_k)$ is determined, according to (68.24) and (68.23), by the formulae

$$\begin{aligned} \hat{a}_k^+ \chi_{n_k'}(n_k) &= \sqrt{n_k' + 1}\, \chi_{n_k'+1}(n_k), \\ \hat{a}_k \chi_{n_k'}(n_k) &= \sqrt{n_k'}\, \chi_{n_k'-1}(n_k), \\ \hat{a}_k \chi_0(n_k) &= 0. \end{aligned} \tag{68.25}$$

A state with any set of numbers n_k can be obtained from the vacuum state $\chi_{0,0,0,\dots}$, in which all occupation numbers are equal to zero by the action of operators $\hat{a}_k^+$ on this state.

In fact,

$$\chi_{n_1', n_2', \dots} = (\hat{a}_1^+)^{n_1'} (\hat{a}_2^+)^{n_2'} \dots \chi_{0,0,0,\dots}.$$

On the other hand, the state with any set of numbers n_k' can be reduced to the vacuum state by the action of operators $\hat{a}_k$:

$$(\hat{a}_1)^{n_1'} (\hat{a}_2)^{n_2'} \dots \chi_{n_1', n_2', \dots} = \chi_{0,0,\dots}.$$

Fermi systems. For a Fermi system the operators $\hat{a}_k$, $\hat{a}_k^+$ obey commutation relations differing from those for boson operators. This predetermines the essential difference in the action of fermion operators on the functions $\chi(n_1, n_2, \dots)$.

Let us also introduce for Fermi systems the eigenfunctions $\chi_{n_k'}(n_k)$ for the operators $\hat{n}_k$. By definition of operator $\hat{n}_k$, we have

$$\hat{n}_k\chi_{n_k'}(n_k) = \hat{a}_k^+\hat{a}_k\chi_{n_k'}(n_k) = n_k'\chi_{n_k'}(n_k). \tag{68.26}$$

Multiplying this equation by $\hat{a}_k^+$ on the left, we obtain by virtue of commutation relations (68.12) an identical zero on the left-hand side of the equation, inasmuch as $(\hat{a}_k^+)^2 = 0$:

$$n_k'\hat{a}_k^+\chi_{n_k'}(n_k) = 0.$$

It follows from here that for all $n_k' \neq 0$, the relation $\hat{a}_k^+\chi_{n_k'}(n_k) = 0$ holds and, in particular, $\hat{a}_k^+\chi_1(n_k) = 0$. At $n_k' = 0$, using relationships (68.12), we obtain

$$\hat{a}_k^+\hat{a}_k\{\hat{a}_k^+\chi_0(n_k)\} = \hat{a}_k^+\chi_0(n_k).$$

Thus, $\hat{a}_k^+\chi_0(n_k)$ is equal to $\chi_1(n_k)$, accurate to some numerical factor.

Applying operator $\hat{a}_k$ to both sides of equation (68.26) and using (68.12), we obtain

$$\hat{a}_k\hat{a}_k^+\hat{a}_k\chi_{n_k'}(n_k) = \hat{a}_k n_k'\chi_{n_k'}(n_k) = n_k'\hat{a}_k\chi_{n_k'}(n_k),$$

whence we conclude that $\hat{a}_k\chi_{n_k'}(n_k) = 0$ for all $n_k' \neq 1$ and, in particular, $\hat{a}_k\chi_0(n_k) = 0$. It is also clear that $\hat{a}_k\chi(n_k)$ is the same as $\chi_0(n_k)$, accurate within some numerical factor, so that

$$\hat{n}_k\hat{a}_k\chi_1(n_k) = \hat{a}_k^+(\hat{a}_k)^2\chi_1(n_k) = 0.$$

Assuming now that there exists a state $\chi_0(n_k)$ in which there are no particles, then, clearly, applying the operators $\hat{a}_k$ and $\hat{a}_k^+$ to this state, we obtain respectively an identical zero $\hat{a}_k\chi_0(n_k) = 0$ and a state with one particle. Applying now the same operators to the state $\chi_1(n_k)$, we obtain only the state $\chi_0(n_k)$ or the identical zero. Thus, it is shown that the commutation relations (68.12) assumed for fermion operators ensure the fulfilment of all main requirements of the Fermi statistics in order that the occupation numbers assumed only the values 0 or 1.

As is the case with Bose systems, any system's state $\chi_{n_1', n_2', \ldots}$ can be obtained from the vacuum state $\chi_{0,0,\ldots}$ by applying the operators $\hat{a}_k^+$. For instance,

$$\chi_{1,0,0,1,0,0,0\ldots} = \hat{a}_1^+\hat{a}_4^+\chi_{0,0,0,0,0,0\ldots}.$$

For this reason $\hat{a}_k^+$ are referred to as creation operators. By analogy, a vacuum state can be obtained from any state $\chi_{n_1', n_2', \ldots}$ by applying the annihilation operators $\hat{a}_k$. For instance

$$\hat{a}_1\hat{a}_2\hat{a}_4\chi_{1,1,0,1,0,\ldots} = \chi_{0,0,0,0,0,\ldots}.$$

To find the explicit form of operators $\hat{a}_k$, $\hat{a}_k^+$, let us first consider a state with a number k, ignoring all other states. The particle creation and annihilation operators for this state, $\hat{\alpha}_k^+$ and $\hat{\alpha}_k$, must satisfy the relationship

$$\hat{\alpha}_k^+\hat{\alpha}_k + \hat{\alpha}_k\hat{\alpha}_k^+ = 1, \quad (\hat{\alpha}_k)^2 = 0, \quad (\hat{\alpha}_k^+)^2 = 0. \tag{68.27}$$

The particle-number operator in the kth state is equal to $\hat{\alpha}_k^+\hat{\alpha}_k$ and its representation is diagonal:

$$\hat{n}_k = \begin{vmatrix} 0 & 0 \\ 0 & 1 \end{vmatrix}. \tag{68.28}$$

The eigenfunctions of $\hat{n}_k$ are the columns $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and the rows (1, 0), (0, 1), describing states without particles and those with one particle in the kth state respectively. The creation and annihilation operators $\hat{\alpha}_k^+$ and $\hat{\alpha}_k$ are described by the equations

$$\hat{\alpha}_k^+\begin{pmatrix} 1 \\ 0 \end{pmatrix} = p\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \hat{\alpha}_k^+\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0,$$

$$\hat{\alpha}_k\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \quad \hat{\alpha}_k\begin{pmatrix} 0 \\ 1 \end{pmatrix} = q\begin{pmatrix} 1 \\ 0 \end{pmatrix},$$

where p and q are arbitrary factors. Solving this system, we find

$$\hat{\alpha}_k^+ = \begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix}, \quad \hat{\alpha}_k = \begin{vmatrix} 0 & 1 \\ 0 & 0 \end{vmatrix}, \quad p = q = 1. \tag{68.29}$$

Just as when considering bosons, we have ignored here insignificant phase factors.

Turning to an examination of the totality of states with different k's, we must introduce operators $\hat{a}_k$ and $\hat{a}_k^+$, satisfying the relations

$$\begin{aligned} &\hat{a}_i^+\hat{a}_k + \hat{a}_k\hat{a}_i^+ = 0 \quad (i \neq k), \\ &\hat{a}_i\hat{a}_k + \hat{a}_k\hat{a}_i = 0, \\ &\hat{a}_i^+\hat{a}_k^+ + \hat{a}_k^+\hat{a}_i^+ = 0, \end{aligned} \tag{68.30}$$

which operators $\hat{\alpha}_k$, $\hat{\alpha}_k^+$ fail to satisfy (in contrast to boson systems where the operators $\hat{a}_k$, $\hat{a}_k^+$, relating to different states, automatically satisfied the necessary commutation relations, since they acted upon different variables).

Let us ascertain that operators

$$\hat{a}_k = (-1)^{\nu_k}\hat{\alpha}_k, \quad \hat{a}_k^+ = (-1)^{\nu_k}\hat{\alpha}_k^+ \tag{68.31}$$

satisfy relationships (68.30). Here ν_k is the number of occupied states, preceding the kth state (the number of occupied states with numbers $i \leqslant k-1$). In fact, for $i > k$, for instance, we have

$$\hat{a}_k^+ \hat{a}_i \chi_{n_1', n_2', \ldots, n_k', \ldots, n_i', \ldots}$$

$$= \begin{cases} \hat{a}_k^+ (-1)^{\nu_i} \chi_{n_1', \ldots, n_k', \ldots, n_i'-1} & \text{at } n_i' = 1, \\ 0 & \text{at } n_i' = 0 \end{cases}$$

$$= \begin{cases} (-1)^{\nu_i + \nu_k} \chi_{n_1', \ldots, n_k'+1, \ldots, n_i'-1, \ldots} & \text{at } n_k' = 0,\ n_i' = 1, \\ 0 & \text{in all remaining cases.} \end{cases}$$

Reversing the order of $\hat{a}_k^+$ and $\hat{a}_l$, we have

$$\hat{a}_l \hat{a}_k^+ \chi_{n_1', \ldots, n_k', \ldots, n_i', \ldots}$$

$$= \begin{cases} \hat{a}_l (-1)^{\nu_k} \chi_{n_1', \ldots, n_k'+1, \ldots, n_i', \ldots} & \text{at } n_k' = 0, \\ 0 & \text{at } n_k' = 1, \end{cases}$$

$$= \begin{cases} (-1)^{\nu_k + \nu_l + 1} \chi_{n_1', \ldots, n_k'+1, \ldots, n_i'-1, \ldots} & \text{at } n_k' = 0,\ n_i' = 1, \\ 0 & \text{in all remaining cases,} \end{cases}$$

since the action of operator $\hat{a}_k^+$ results in the number of occupied states, "preceding" the ith state, increasing by 1. Hence,

$$(\hat{a}_k^+ \hat{a}_l + \hat{a}_l \hat{a}_k^+) \chi = 0.$$

In this way, for a fermion system, operators $\hat{a}_k$, $\hat{a}_k^+$, $\hat{a}_l$, $\hat{a}_l^+$ are not independent, each of these operators depending on whether the number of occupied states preceding k is even or odd. It is readily seen that the action of operators $\hat{a}_k$ and $\hat{a}_k^+$ on function $\chi_{n_k'}(n_k)$ is determined, according to relations (68.29), (68.31), by the formulae

$$\begin{aligned} \hat{a}_k \chi_{n_k'}(n_k) &= \begin{cases} (-1)^{\nu_k} \sqrt{n_k'}\, \chi_{n_k'-1}(n_k) & \text{at } n_k' = 1, \\ 0 & \text{at } n_k' = 0, \end{cases} \\ \hat{a}_k^+ \chi_{n_k'}(n_k) &= \begin{cases} (-1)^{\nu_k} \sqrt{1 - n_k'}\, \chi_{n_k'+1}(n_k) & \text{at } n_k' = 0, \\ 0 & \text{at } n_k' = 1. \end{cases} \end{aligned} \tag{68.32}$$

Knowing the physical meaning of the Bose- and Fermi operators $\hat{a}_k$, $\hat{a}_k^+$, we see that by virtue of the formulae

$$\hat{\psi}(\mathbf{r}) = \sum_k \hat{a}_k \varphi_k(\mathbf{r}), \quad \hat{\psi}^+(\mathbf{r}) = \sum_k \hat{a}_k^+ \varphi_k^*(\mathbf{r})$$

operators $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}^+(\mathbf{r})$ have the meaning of creation and annihilation operators at a given space point.

Let us consider an operator of some physical quantity $\hat{\mathcal{A}}$, assuming the quantity to be additive:

$$\hat{\mathcal{A}} = \sum_k \hat{A}_k \tag{68.33}$$

(summation is carried out over all system's particles). All the operators $\hat{A}_k$ are assumed to be similar, but applied to the coordinate wave functions of different particles. Quantities of this type are the momentum, angular momentum, kinetic energy, charge, etc.

It will be shown that in occupation representation the operator $\hat{\mathcal{A}}$ can be presented by means of the secondary quantized wave function $\psi(\mathbf{r})$ in the following manner:

$$\hat{\mathfrak{A}} = \int \hat{\psi}^+(\mathbf{r})\, \hat{A}\hat{\psi}(\mathbf{r})\, d^3r. \tag{68.34}$$

To prove that, let us express operator $\hat{\mathfrak{A}}$ in terms of particle-number operators $\hat{n}_k$ in the states corresponding to definite values A_s of the quantity A. It is clear that

$$\hat{\mathfrak{A}} = \sum_s A_s \hat{n}_s. \tag{68.35}$$

On the other hand, we expand the operator wave function $\hat{\psi}(\mathbf{r})$ in eigenfunctions $\varphi_s(\mathbf{r})$ of the operator $\hat{A}$:

$$\hat{\psi}(\mathbf{r}) = \sum_s \hat{a}_s \varphi_s(\mathbf{r}), \quad \hat{A}\varphi_s(\mathbf{r}) = A_s \varphi_s(\mathbf{r}).$$

Substituting this expansion into the right-hand side of Eq. (68.34) and using the orthonormality of the system $\varphi_s(\mathbf{r})$, we obtain

$$\hat{\mathfrak{A}} = \sum_{r,\,s} \hat{a}_r^+ \hat{a}_s A_s \int \varphi_r^*(\mathbf{r})\, \varphi_s(\mathbf{r})\, d^3r = \sum_s A_s \hat{n}_s.$$

Formulae (68.34) and (68.35) express the operator $\hat{\mathfrak{A}}$ in a representation of occupation numbers of states with different values of A_s, whereas formula (68.33) expresses the same $\hat{\mathfrak{A}}$ operator in a coordinate representation. The operator can of course be expressed in any other representation.

Let $\hat{B}$ be the operator of any single-particle physical quantity, $\varphi_s(\mathbf{r})$ the eigenfunctions of the operator, and $\hat{a}_s^+$, $\hat{a}_s$ the creation and annihilation operators pertaining to the state $\varphi_s(\mathbf{r})$. Presenting the operator wave function in the form of the superposition $\hat{\psi}(\mathbf{r}) = \sum_s \hat{a}_s \varphi_s(\mathbf{r})$ and using the orthonormality of $\varphi_s(\mathbf{r})$, we obtain from

formula (68.35)

$$\hat{\mathfrak{A}} = \sum_{s,\, s'} A_{ss'} \hat{a}_s^+ \hat{a}_{s'}, \tag{68.36}$$

where $A_{ss'} = \int \varphi_s^* (\mathbf{r}) \hat{A} \varphi_{s'}(\mathbf{r})\, d^3r$ are the matrix elements of the operator $\hat{A}$ in B-representation.

Of special interest is the occupation-number representation associated with momentum. Since in statistical physics the volume of gas is of essential importance, below we shall study particles not in infinite motion, but confined within a cubic box of volume $V = L^3$.

In Secs. 68 through 70, instead of Planck's constant h, the constant $\hbar = \frac{h}{2\pi}$, associated with it, will be used. Further, for the sake of simplicity, the wave vector of a particle $\mathbf{k} = \mathbf{p}/\hbar$ will be called momentum. In this case the functions $e^{i\mathbf{pr}/\hbar} = e^{i\mathbf{kr}}$, the eigenfunctions of the momentum operator $-i\hbar\nabla$, will not be such for finite motion, since they do not vanish at the walls of the box. The physical meaning of this is that for a particle in the box the momentum does not assume a definite value—at a given energy E the momentum can acquire with an equal probability the values $\pm \sqrt{2mE}$. We shall nevertheless expand all coordinate-dependent functions in functions

$$\varphi_{\mathbf{k}} (\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{kr}}, \tag{68.37}$$

where $1/\sqrt{V}$ has the meaning of a normalizing factor. Let us impose on $\varphi_{\mathbf{k}}(\mathbf{r})$ the following periodic boundary conditions: a whole number of de Broglie waves must be arranged along one edge of the cube, i.e. the condition $k_i = 2\pi n_i/L$, where $n_i = 0, 1, 2, \ldots$, must be satisfied for any momentum projection. It can be readily seen that these conditions determine the quantized values of particle energy in the box (see Sec. 45). The orthogonality condition for the two functions $\varphi_{\mathbf{k}}(\mathbf{r})$ and $\varphi_{\mathbf{k}'}(\mathbf{r})$ can be presented in the form

$$\int \varphi_{\mathbf{k}}^* (\mathbf{r})\, \varphi_{\mathbf{k}'} (\mathbf{r})\, d^3r = \frac{1}{V} \int e^{i(\mathbf{k}'-\mathbf{k},\, \mathbf{r})}\, d^3r = \delta_{\mathbf{k},\, \mathbf{k}'}, \tag{68.38}$$

where $\delta_{\mathbf{k},\, \mathbf{k}'}$ is the analogue of the Kronecker delta used in algebra.

Let the operator $\hat{A}$ be the operator of an external field $\mathcal{U}(\mathbf{r})$. We denote by $\hat{a}^+(\mathbf{k})$ and $\hat{a}(\mathbf{k})$ the creation and annihilation operators for particles with momentum $\mathbf{k}$. Then, by formula (68.36) we find in an occupation-number representation

$$\hat{\mathfrak{A}} = V^{-1} \sum_{\mathbf{k},\, \mathbf{k}'} u(\mathbf{k}-\mathbf{k}')\, \hat{a}^+(\mathbf{k}')\, \hat{a}(\mathbf{k}), \tag{68.39}$$

where $u(\mathbf{q}) = \int \mathcal{U}(\mathbf{r}) e^{i\mathbf{qr}} d^3r$ is the Fourier component of the potential $\mathcal{U}(\mathbf{r})$.

In the representation under consideration the secondary quantized operator of kinetic energy $\hat{K} = \sum_i \frac{\hat{p}_i^2}{2m}$ acquires the form

$$\hat{\mathcal{K}} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} \hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} \hat{n}(\mathbf{k}). \tag{68.40}$$

Similarly, we can take the two-particle operator $\hat{B}$:

$$\hat{B} = \frac{1}{2} \sum_{i \neq j} \hat{B}_{ij} \tag{68.41}$$

(summation over i, j is performed for system's particles). As in the case considered above, all operators $\hat{B}_{ij}$ are assumed to be the same, but acting on the coordinate wave functions of different particles. The most important example of an operator of this kind is the total energy of interaction, $\hat{H}_{\text{int}}$, of a system of particles with pair interaction. If pair interaction is described by potential $\mathscr{W}(r_{ij})$, then the formula for $\hat{H}_{\text{int}}$ is

$$\hat{H}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \mathscr{W}(r_{ij}). \tag{68.42}$$

Omitting similar calculations, we write down the expression for $\hat{H}_{\text{int}}$ in terms of $\hat{\psi}(r)$:

$$\hat{\mathscr{H}}_{\text{int}} = \frac{1}{2} \int\int \hat{\psi}^+(\mathbf{r}_1)\,\hat{\psi}^+(\mathbf{r}_2)\,\mathscr{W}(r_{12})\,\hat{\psi}(\mathbf{r}_2)\,\hat{\psi}(\mathbf{r}_1)\,d^3r_1\,d^3r_2, \tag{68.43}$$

or in an occupation-number representation

$$\hat{\mathscr{H}}_{\text{int}} = \frac{1}{2V^2} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2'} w(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2')\,\hat{a}^+(\mathbf{k}_1')\,\hat{a}^+(\mathbf{k}_2')\,\hat{a}(\mathbf{k}_2)\,\hat{a}(\mathbf{k}_1), \tag{68.44}$$

where

$$w(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2') = \int \mathscr{W}(r_{12})\, e^{i(\mathbf{k}_1\mathbf{r}_1 + \mathbf{k}_2\mathbf{r}_2 - \mathbf{k}_1'\mathbf{r}_1 - \mathbf{k}_2'\mathbf{r}_2)}\, d^3r_1\, d^3r_2. \tag{68.45}$$

Turning now to new integration variables

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \quad \mathbf{r}_1 = \mathbf{R} - \frac{\mathbf{r}}{2}, \quad \mathbf{r}_2 = \mathbf{R} + \frac{\mathbf{r}}{2},$$

we obtain

$$w(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2') = \int \mathscr{W}(r)\, e^{i(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{k}_1' - \mathbf{k}_2')\mathbf{r}/2}\, d^3r \int e^{i(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_1' - \mathbf{k}_2', \mathbf{R})}\, d^3R.$$

Making use of the orthonormality condition (68.38), we obtain $w(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2')$

$$= V\delta_{\mathbf{k}_1+\mathbf{k}_2,\, \mathbf{k}_1'+\mathbf{k}_2'} \int \mathscr{W}(r)\, e^{i(\mathbf{k}_2-\mathbf{k}_1+\mathbf{k}_1'-\mathbf{k}_2')r/2}\, d^3r. \quad (68.46)$$

The presence of the δ-symbol indicates that the vector $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_1'$, $\mathbf{k}_2'$ must form a closed quadrangle. As is seen from Fig. 90,

$$\mathbf{k}_1' = \mathbf{k}_1 + \mathbf{k}, \quad \mathbf{k}_2' = \mathbf{k}_2 - \mathbf{k}, \quad \mathbf{k} = \mathbf{k}_1' - \mathbf{k}_1 = \mathbf{k}_2 - \mathbf{k}_2', \quad (68.47)$$
$$\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{k}_1' - \mathbf{k}_2' = 2\mathbf{k},$$

i.e. the law of conservation of momentum is obeyed during collision.

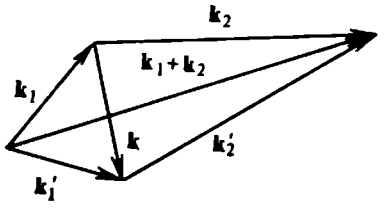


FIG. 90

If the notation

$$w(k) = \int \mathscr{W}(r)\, e^{ikr}\, d^3r, \quad (68.48)$$

is introduced, formula (68.46) reduces to

$$w(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_1', \mathbf{k}_2')$$
$$= Vw(k)\, \delta_{\mathbf{k}_1+\mathbf{k}_2,\, \mathbf{k}_1'+\mathbf{k}_2'}. \quad (68.49)$$

The Hamiltonian of a system of interacting particles $\hat{\mathscr{H}}$ in the absence of an applied field is equal to

$$\hat{\mathscr{H}} = \hat{\mathscr{K}} + \hat{\mathscr{H}}_{\text{int}} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m}\, \hat{a}^+(\mathbf{k})\, \hat{a}(\mathbf{k})$$
$$+ \frac{1}{2V} \sum_{\mathbf{k}_1,\, \mathbf{k}_2,\, \mathbf{k}_1',\, \mathbf{k}_2'} w(k)\, \delta_{\mathbf{k}_1+\mathbf{k}_2,\, \mathbf{k}_1'+\mathbf{k}_2'} \hat{a}^+(\mathbf{k}_1')\, \hat{a}^+(\mathbf{k}_2')\, \hat{a}(\mathbf{k}_2)\, \hat{a}(\mathbf{k}_1).$$

The δ-symbol can be eliminated from this expression by means of formula (68.47):

$$\hat{\mathscr{H}} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m}\, \hat{a}^+(\mathbf{k})\, \hat{a}(\mathbf{k})$$
$$+ \frac{1}{2V} \sum_{\mathbf{k}_1,\, \mathbf{k}_2,\, \mathbf{k}} w(k)\, \hat{a}^+(\mathbf{k}_1 + \mathbf{k})\, \hat{a}^+(\mathbf{k}_2 - \mathbf{k})\, \hat{a}(\mathbf{k}_2)\, \hat{a}(\mathbf{k}_1). \quad (68.50)$$

In conclusion, let us derive the formula for the probability of transition from one state to another in an ideal Bose- or Fermi gas under the influence of an external effect. Such effects can be produced by an external field or by interaction with particles of different kind, such as admixture atoms, lattice ions, etc. As is known from quantum mechanics, in a perturbation theory representation the transition probability density per unit time is determined by the formula (see,

for instance, [7])

$$P_{if} = \frac{2\pi}{\hbar} |\mathcal{U}_{if}|^2 \delta (E_f - E_i), \tag{68.51}$$

where the index i denotes the initial, and the index f the final state of the system; $\mathcal{U}_{if}$ is the matrix perturbation element provoking the transition, and the factor $\delta (E_f - E_i)$ ensures the fulfilment of the law of conservation of energy. According to formula (68.39), we have

$$\hat{\mathfrak{U}} = \frac{1}{V} \sum_{k,\, k'} u (|k - k'|) \hat{a}^+ (k') \hat{a} (k).$$

The operators $\hat{a}^+(k')$ and $\hat{a}(k)$ have nonzero matrix elements only for transitions in which one particle with momentum k vanishes and one particle with momentum k' is created, i.e. inelastic scattering of a particle, associated with the change in momentum, takes place.

Using formulae (68.25), (68.32), we obtain

$$P_{if} = \sum_{k,\, k'} \sigma (k,\, k')\, n (k) [1 \pm n (k')] \delta [E (k') - E (k)], \tag{68.52}$$

where the upper sign pertains to a Bose gas, and the lower sign to a Fermi gas. The quantity $\sigma (k, k')$ is the product of $u (|k - k'|)$ and all constant factors. In the case of a Fermi gas formula (68.52) presents another illustration of Pauli's exclusion principle: if the state k is occupied, i.e. $n (k') = 1$, the contribution of this state to the transition probability is equal to zero. In the case of a Bose gas the factor $1 + n (k')$ indicates that bosons tend to accumulate in one state. The greater $n (k')$, the greater the probability of bosons passing to that state. This property is directly associated with the Bose condensation—the accumulation of bosons in zero-energy states at $T \to 0$.

69*. Superfluidity. Bogoliubov's Theory

Let us consider the model of a non-ideal Bose gas characterized by pairwise interaction of particles of the kind (68.42). This model is described in a second-quantization representation by the Hamiltonian

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} E (\mathbf{k}) \hat{a}^+ (\mathbf{k}) \hat{a} (\mathbf{k}) + \frac{1}{2V} \sum_{\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'} w (|\mathbf{k}_1' - \mathbf{k}_1|) \hat{a}^+ (\mathbf{k}_1') \hat{a}^+ (\mathbf{k}_2') \hat{a} (\mathbf{k}_2) \hat{a} (\mathbf{k}_1), \tag{69.1}$$

where $E (k) = \frac{\hbar^2 k^2}{2m}$.

For an ideal gas in the vicinity of absolute zero the predominant number of particles N_0 is in the state $k = 0$, and the Einstein con-

densation takes place:

$$N - N_0 \ll N_0. \tag{69.2}$$

Inequality (69.2) is assumed to be also valid for a weakly non-ideal Bose gas. Then, in the second of the equations

$$\hat{a}^+(0)\,\hat{a}(0)\,\chi_{N_0} = N_0\chi_{N_0}, \qquad \hat{a}(0)\,\hat{a}^+(0) = (N_0+1)\,\chi_{N_0}$$

we can assume approximately $N_0 + 1 \approx N_0$. Operators $\hat{a}^+(0)$ and $\hat{a}(0)$ then turn into commutative operators, and we shall assume them to be numbers, equal to

$$a^+(0) = a(0) = N_0^{1/2}. \tag{69.3}$$

Condition (69.2) shows that most particles are in the condensate. Evidently, only the interaction of these particles with the "overcondensate" particles should be accounted for in Hamiltonian (69.1). The interaction of "overcondensate" particles with each other will be ignored. The theory of a weakly non-ideal Bose gas, based on these assumptions, was suggested by N. N. Bogoliubov [52].

Let us single out in operator $\hat{\mathscr{H}}_{\text{int}}$ the terms containing $a^+(0)$ and $a(0)$. Allowing for the momentum conservation law (the prime at the summation sign indicates that the term with $k = 0$ is omitted), we obtain

$$\begin{aligned}\hat{\mathscr{H}}_{\text{int}} = \frac{1}{2V}\Big\{ & w(0)\,[a^+(0)\,a(0)]^2 \\ & + \sum_{\mathbf{k}}{}' [w(0)+w(k)]\,[\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{a}^+(-\mathbf{k})\,\hat{a}(-\mathbf{k})]\,a^+(0)\,a(0) \\ & + \sum_{\mathbf{k}}{}' w(k)\,\{[a(0)]^2\,\hat{a}^+(\mathbf{k})\,\hat{a}^+(-\mathbf{k}) + [a^+(0)]^2\,\hat{a}(\mathbf{k})\,\hat{a}(-\mathbf{k})\} \\ & + \text{terms linear in } a^+(0) \text{ or } a(0), \\ & + \text{terms not containing } a^+(0) \text{ and } a(0)\Big\}.\end{aligned}$$

For our purposes it is convenient to write the expression

$$2\sum_{\mathbf{k}}{}' [w(0)+w(k)]\,\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k})\,a^+(0)\,a(0)$$

in the form

$$\sum_{\mathbf{k}}{}' [w(0)+w(k)]\,[\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{a}^+(-\mathbf{k})\,a(-\mathbf{k})]\,a^+(0)\,a(0).$$

Leaving terms containing N_0 to not less than the first power, we obtain

$$\begin{aligned}\hat{\mathscr{H}}_{\text{int}} = \frac{1}{2V}\Big\{ & N_0^2 w(0) + N_0 \sum_{\mathbf{k}} [w(0)+w(k)]\,[\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) \\ & + \hat{a}^+(-\mathbf{k})\,\hat{a}(-\mathbf{k})] + N_0 \sum_{\mathbf{k}}{}' w(k)\,[\hat{a}^+(\mathbf{k})\,\hat{a}^+(-\mathbf{k}) + \hat{a}(\mathbf{k})\,\hat{a}(-\mathbf{k})]\Big\}.\end{aligned} \tag{69.4}$$

The number of particles is expressed by

$$\hat{N} = N_0 + \frac{1}{2} \sum_{\mathbf{k}}{}' [\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{a}^+(-\mathbf{k})\,\hat{a}(-\mathbf{k})]. \tag{69.5}$$

Substituting the expression for N_0 (69.5) into formula (69.4) and ignoring the terms not containing N, we obtain

$$\hat{\mathcal{H}}_{\text{int}} = \frac{1}{2V}\Big\{N^2 w(0) + N \sum_{\mathbf{k}}{}' w(k)\,[\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{a}^+(-\mathbf{k})\,\hat{a}(-\mathbf{k})] + N \sum_{\mathbf{k}}{}' w(k)\,[\hat{a}^+(\mathbf{k})\,\hat{a}^+(-\mathbf{k}) + \hat{a}(\mathbf{k})\,\hat{a}(-\mathbf{k})]\Big\}.$$

The energy operator is expressed by

$$\hat{\mathcal{H}} = \frac{w(0)\,N^2}{2V} + \frac{1}{2} \sum_{\mathbf{k}}{}' \left[E(k) + \frac{w(k)\,N}{V}\right][\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{a}^+(-\mathbf{k})\,\hat{a}(-\mathbf{k})] + \frac{1}{2} \sum_{\mathbf{k}}{}' \frac{w(k)\,N}{V}[\hat{a}^+(\mathbf{k})\,\hat{a}^+(-\mathbf{k}) + \hat{a}(\mathbf{k})\,\hat{a}(-\mathbf{k})]. \tag{69.6}$$

The third term in expression (69.6) describes the possible creation or annihilation of a pair of particles with momenta $\mathbf{k}$ and $-\mathbf{k}$. The physical meaning of this is that such pairs may pass from a "condensate" (a state with $k = 0$ and $E(k) = 0$) to a state with nonzero momentum and energy, and vice versa, when the momentum conservation law is observed. The possibility of such processes is associated with the interaction of "overcondensate" particles with "condensate" particles.

Let us pass now from Bose operators $\hat{a}(\mathbf{k})$ and $\hat{a}^+(\mathbf{k})$ to new Bose operators $\hat{\xi}(\mathbf{k})$ and $\hat{\xi}^+(\mathbf{k})$ by means of the Bogoliubov canonical transformation to ensure diagonalization of Hamiltonian (69.6)

$$\begin{aligned}
\hat{a}(\mathbf{k}) &= \hat{\xi}(\mathbf{k}) \cosh \varphi(k) + \hat{\xi}^+(-\mathbf{k}) \sinh \varphi(k),\\
\hat{a}^+(\mathbf{k}) &= \hat{\xi}^+(\mathbf{k}) \cosh \varphi(k) + \hat{\xi}(-\mathbf{k}) \sinh \varphi(k),\\
\hat{a}(-\mathbf{k}) &= \hat{\xi}(-\mathbf{k}) \cosh \varphi(k) + \hat{\xi}^+(\mathbf{k}) \sinh \varphi(k),\\
\hat{a}^+(-\mathbf{k}) &= \hat{\xi}^+(-\mathbf{k}) \cosh \varphi(k) + \hat{\xi}(\mathbf{k}) \sinh \varphi(k),
\end{aligned} \tag{69.7}$$

where $\varphi(k)$ is a real parameter depending only on module of $\mathbf{k}$. It is easy to verify that the commutation relations for operators $\hat{a}(\mathbf{k})$, $\hat{a}'(\mathbf{k})$, are also valid for operators $\hat{\xi}(\mathbf{k})$, $\hat{\xi}^+(\mathbf{k})$:

$$\begin{aligned}
\hat{\xi}(\mathbf{k})\,\hat{\xi}(\mathbf{k}') - \hat{\xi}(\mathbf{k}')\,\hat{\xi}(\mathbf{k}) &= 0,\\
\hat{\xi}^+(\mathbf{k})\,\hat{\xi}^+(\mathbf{k}') - \hat{\xi}^+(\mathbf{k}')\,\hat{\xi}^+(\mathbf{k}) &= 0,\\
\hat{\xi}(\mathbf{k})\,\hat{\xi}^+(\mathbf{k}') - \hat{\xi}^+(\mathbf{k}')\,\hat{\xi}(\mathbf{k}) &= \delta_{\mathbf{k},\mathbf{k}'}.
\end{aligned}$$

This permits operators $\hat{\xi}^+(\mathbf{k})$, $\hat{\xi}(\mathbf{k})$ to be considered as creation and annihilation operators for new Bose quasi-particles, and operators $\hat{\xi}^+(\mathbf{k})$. $\hat{\xi}(\mathbf{k})$ as occupation-number operators. When expressed in terms of the new operators $\hat{\xi}(\mathbf{k})$ and $\hat{\xi}^+(\mathbf{k})$, the energy operator acquires the following form:

$$\hat{\mathscr{H}} = \frac{w(0)N^2}{2V} + \frac{1}{2}\sum_{\mathbf{k}}{}' \left\{\left[E(k) + \frac{w(k)N}{V}\right][\cosh 2\varphi(k) - 1]\right.$$
$$\left. + \frac{w(k)N}{V}\sinh 2\varphi(k)\right\} + \frac{1}{2}\sum_{\mathbf{k}}{}' \left\{\left[E(k) + \frac{w(k)N}{V}\right]\cosh 2\varphi(k)\right.$$
$$\left. + \frac{w(k)N}{V}\sinh 2\varphi(k)\right\}[\hat{\xi}^+(\mathbf{k})\hat{\xi}(\mathbf{k}) + \hat{\xi}^+(-\mathbf{k})\hat{\xi}(-\mathbf{k})]$$
$$+ \frac{1}{2}\sum_{\mathbf{k}}{}' \left\{\left[E(k) + \frac{w(k)N}{V}\right]\sinh 2\varphi(k)\right.$$
$$\left. + \frac{w(k)N}{V}\cosh 2\varphi(k)\right\}[\hat{\xi}^+(\mathbf{k})\hat{\xi}^+(-\mathbf{k}) + \hat{\xi}(\mathbf{k})\hat{\xi}(-\mathbf{k})].$$

Let us now select the parameter $\varphi(k)$ so that the last term vanishes. In this case, in the quasi-particle number representation the Hamiltonian becomes diagonal. The terms describing transitions involving particle creation or annihilation vanish, and the diagonal elements of operator $\hat{\mathscr{H}}$ determine the gas energy spectrum. The physical meaning of this is that from the picture of a real gas of interacting particles with creation and annihilation operators $\hat{a}^+(\mathbf{k})$, $\hat{a}(\mathbf{k})$ we pass to the picture of an ideal gas of non-interacting particles with operators $\hat{\xi}^+(\mathbf{k})$, $\hat{\xi}(\mathbf{k})$.

The Hamiltonian can be transformed to the new variables by means of the following readily proved relationship. If

$$p\sinh\psi + q\cosh\psi = 0,$$

then

$$p\cosh\psi + q\sinh\psi = \sqrt{p^2 - q^2}.$$

We have

$$\hat{\mathscr{H}} = \frac{w(0)N^2}{2V} - \frac{1}{2}\sum_{\mathbf{k}}{}' \left\{E(k) + \frac{w(k)N}{V}\right.$$
$$\left. - \sqrt{\left[E(k) + \frac{w(k)N}{V}\right]^2 - \left[\frac{w(k)N}{V}\right]^2}\right\}$$
$$+ \frac{1}{2}\sum_{\mathbf{k}}{}' \sqrt{\left[E(k) + \frac{w(k)N}{V}\right]^2 - \left[\frac{w(k)N}{V}\right]^2}$$
$$\times [\hat{\xi}^+(\mathbf{k})\hat{\xi}(\mathbf{k}) + \hat{\xi}^+(-\mathbf{k})\hat{\xi}(-\mathbf{k})]. \quad (69.8)$$

Introducing the notation

$$\omega(k) = \sqrt{\left[\frac{\hbar^2 k^2}{2m} + \frac{w(k)N}{V}\right]^2 - \left[\frac{w(k)N}{V}\right]^2} = \sqrt{\frac{\hbar^4 k^4}{4m^2} + \frac{\hbar^2 k^2 w(k) N}{mv}}, \quad (69.9)$$

we finally obtain

$$\hat{\mathcal{H}} = \frac{w(0)N^2}{2V} - \frac{1}{2}\sum_{\mathbf{k}}{}' \left[E(k) + \frac{w(k)N}{V} - \omega(k)\right] + \frac{1}{2}\sum_{\mathbf{k}}{}' \omega(k)\left[\hat{\xi}^+(\mathbf{k})\hat{\xi}(\mathbf{k}) + \hat{\xi}^+(-\mathbf{k})\hat{\xi}(-\mathbf{k})\right]. \quad (69.10)$$

It is clear that close to absolute zero the energy of a weakly non-ideal gas can be represented as the sum of the ground-state energy—the first two terms in Eq. (69.10), and the energy of independent quasi-particles whose energy is $\omega(k)$.

Let us examine the dependence of the energy of quasi-particles ω on momentum at large and small values of k.

For small values of k formula (69.9) yields

$$\omega(k) \approx \sqrt{\frac{Nw(k)}{mV}}\hbar k \approx \sqrt{\frac{Nw(0)}{mV}}\hbar k, \quad (69.11)$$

i.e. at small momenta the quasi-particles behave as phonons with sound velocity equal to $\sqrt{Nw(0)/mV}\hbar$.

At large values of k the dependence $\omega(k)$ is primarily determined by the properties of the function $w(k)$. In particular, the interaction $w(k)$ can be so chosen as to obtain the quasi-particle energy spectrum, suggested by L. D. Landau from phenomenological considerations [18] and agreeing well with the experimental data on the heat capacity and other thermodynamic properties of HeII. This energy spectrum is shown in Fig. 91.

Assuming that at large values of k the function $w(k)$ decreases or increases at a slower rate than k^2, then we obtain for $\omega(k)$

$$\omega(k) \approx \frac{\hbar^2 k^2}{2m} + w(k)\frac{N}{V} \approx \frac{\hbar^2 k^2}{2m}, \quad (69.12)$$

i.e. with large values of k quasi-particles behave as classical particles of mass m.

Let us show that a quasi-particle gas, obeying the dispersion law $\omega(k)$, possesses the property of *superfluidity*. This means that neither the friction against the walls of a tube or the surface of any body moving with respect to the gas, nor the internal friction in the gas can lead to deceleration of the flow and conversion of the kinetic energy of the flow into the excitation energy. Let us consider the gas at

$T = 0$, so that there is no quasi-particle excitation in it. Since momentum $\mathbf{k}$ and energy $\omega(k)$ of quasi-particles are determined in a stationary medium, the gas will be assumed to be at rest, and the walls of the tube or the body placed in the gas to be moving with respect to the gas with velocity $\mathbf{v}$.

Let us assume that a body lost momentum $\Delta\mathbf{P}$ and energy ΔE and some number of quasi-particles $n(\mathbf{k})$ with various momenta $\mathbf{k}$ appeared in the gas at the expense of these losses; then

$$\Delta\mathbf{P} = \sum_{\mathbf{k}} n(\mathbf{k})\,\hbar\,\mathbf{k}, \quad \Delta E = \sum_{\mathbf{k}} n(\mathbf{k})\,\omega(k).$$

On the other hand, the change in energy and momentum of a moving body is expressed by

$$\Delta E = (\mathbf{v}, \Delta\mathbf{P}), \tag{69.13}$$

whence

$$\sum_{\mathbf{k}} n(\mathbf{k})\,[\omega(k) - \hbar(\mathbf{vk})] = 0. \tag{69.14}$$

Since Eq. (69.14) must be satisfied for arbitrary $n(\mathbf{k})$, we have $\omega(k) = \hbar(\mathbf{vk}) = \hbar vk\cos(\widehat{\mathbf{vk}})$, with $\cos(\widehat{\mathbf{vk}}) > 0$:

$$v = \frac{\omega(k)}{\hbar k\cos(\widehat{\mathbf{vk}})}, \quad v \geqslant \frac{\omega(k)}{\hbar k} = v_{\mathrm{cr}}. \tag{69.15}$$

When the dispersion law (69.9) is valid, the right-hand side of Eq. (69.15), which is the ratio of the ordinate of the curve shown in Fig. 92 to its abscissa, differs from zero.

This means that there exists a critical flow velocity v_{cr}, equal to sound velocity $v_s = \sqrt{Nw''(0)/mV}\,\hbar$, such that at velocities lower

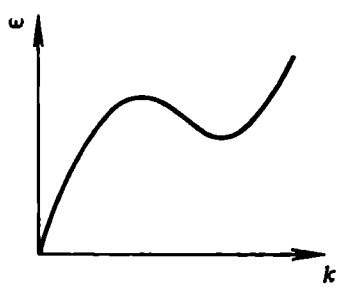


FIG. 91

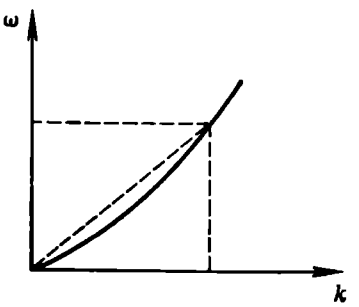


FIG. 92

than the critical the flow deceleration at the expense of the appearance of quasi-particles is impossible, i.e. there is no internal friction in the gas. It should be noted that the critical velocity differing from zero always exists when the curve $\omega(k)$ is not tangent to the x-axis

at the origin of coordinates (the contact with the x-axis at other points is highly improbable), i.e. at small values of k the energy spectrum is of a phonon nature, $\omega = v_s k$. The spectrum depicted in Fig. 91 also possesses this property.

At temperatures differing from zero the motion of a non-ideal Bose gas can be considered as the superposition of two motions. The totality of quasi-particles with energy $\omega(k)$ present in the gas at $T \neq 0$ is capable of exchanging energy and momentum with the walls as a "normal" liquid. The totality of "non-excited" quasi-particles move in the tube at $v < v_{cr}$ as a superfluid liquid, since the processes involving the appearance of new quasi-particles in it are impossible. The absence of quasi-particles was nowhere assumed in the proof presented above, and it also remains valid at $T \neq 0$. There is no "friction" between the normal and superfluid components, since energy and momentum are not transferred from one component to the other—quasi-particle creation and annihilation processes are impossible.

It should be, however, emphasized that we can speak about the "normal" and "superfluid" components of a liquid only in some conditional sense. No division of atoms into "normal" and "superfluid", naturally, exists and we speak about the collective motions of liquid particles or quasi-particles. As temperature approaches the phase-transition temperature, all collective degrees of freedom are excited, the liquid is "filled up" with quasi-particles and becomes "normal". On the contrary, as temperature approaches zero, the quasi-particles vanish, and liquid becomes "superfluid".

A more detailed treatment of the theory of superfluidity is given in [19] and especially in [20]. The latter book presents the rather attractive, mainly qualitative, theory of superfluidity elaborated by Feynman.

It is interesting to note that Bogoliubov's theory [52] leads to an energy spectrum of the Landau type when $w(k)$ is simply chosen as a linear function of k:

$$w(k) = A - Bk, \tag{69.16}$$

where A and B are constants.

According to formula (69.9), the energy of a quasi-particle is determined by the expression

$$\omega(k) = \sqrt{\frac{\hbar^4 k^4}{4m^2} - \frac{\hbar^2 N B k^3}{mV} + \frac{\hbar^2 N A k^2}{mV}}. \tag{69.17}$$

The Fourier-transform of potential (69.16) can be shown to correspond in the coordinate space to the superposition of delta-shaped repulsion and repulsion $\sim r^{-4}$. This result should not be, however, overestimated, since it has not been fully established whether the use of Fourier's coefficients $w(k)$ instead of $w(0)$ in the calculations of this section resulted in a surpassing accuracy.

Problems

1. Show that the function (69.17) has a minimum and a maximum (under which conditions?). Express the parameters Δ_0, k^*, m^* in the Landau formula $\omega(k) = \Delta_0 + \frac{(k-k^*)^2}{2m^*}$, which is valid in the vicinity of the minimum $\omega(k)$, in terms of the constants A and B from formula (69.17).
2. Show that the potential $W(r)$, a superposition of the delta-shaped repulsion and the repulsion $\sim r^{-4}$, corresponds to the Fourier-transform presented by formula (69.16).

70*. Superconductivity

Let us consider the theory of superconductivity as another example of application of the method of second quantization.

A clue to the comprehension of superconductivity of metals is the interaction of electrons with crystal lattice vibrations. Quantum mechanics describes this interaction as the emission or absorption of phonons by electrons. These processes can be shown (see [21], for instance) to cause effective electron interaction in addition to their Coulomb repulsion. As this takes place, the effective interaction between electrons differs markedly from zero only for electrons whose momentum is close to the Fermi momentum $k_{max} = p_{max}/\hbar$.

It can be shown that the interaction between electrons with momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ must be accounted for only when the ends of the vectors of $\mathbf{k}_1$ and $\mathbf{k}_2$ lie in the spherical layer close to the Fermi sphere, with a thickness of the order of ν_D/v_{max}, where ν_D is the Debye frequency and v_{max} is the Fermi velocity. If at least one of the momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ emerges from the above-indicated layer, the electron interaction becomes negligible. For electrons whose momenta are arranged inside this layer the interaction is of the attraction nature and it is said to be short-range interaction in a coordinate representation. For this reason this interaction is of importance only to electrons with spin projections of opposite signs, since the probability that the electrons will draw closer than the range of interaction is very small for electrons with parallel spins. Finally, the main contribution to interaction can be shown to be made by pairs of electrons with zero total momentum. The reason for this can readily be grasped examining Fig. 93.

The figure shows a Fermi sphere, and the effectively interacting electrons have momenta almost equal to k_{max} (the end points of momentum vectors lie in the narrow layer close to the Fermi sphere). Then, if the total momentum $\mathbf{k}$ of an electron pair differs from zero [Fig. 93 (*a*)], the ends of vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ must lie on the opposite edges of torus L and they fill the one-dimensional set of points. The

ends of vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ of electron pairs with a total momentum equal to zero can lie anywhere on the diametrically opposite points of the Fermi sphere [Fig. 93 (*b*)] and fill a "two-dimensional" set of points. Thus, ignoring the Coulomb's repulsion and accounting for the effective attraction between electrons with opposite momenta and spin projections with opposite signs, we come to the model Hamiltonian

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} E(k) [\hat{a}^+(\mathbf{k}) \hat{a}(\mathbf{k}) + \hat{b}^+(\mathbf{k}) \hat{b}(\mathbf{k})]$$

$$- \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} w(\mathbf{k}, \mathbf{k}') \hat{a}^+(\mathbf{k}) \hat{b}^+(-\mathbf{k}) \hat{b}(-\mathbf{k}') \hat{a}(\mathbf{k}'). \quad (70.1)$$

In formula (70.1) $E(k) = \frac{\hbar^2 k^2}{2m}$, $\hat{a}^+(\mathbf{k})$, $\hat{a}(\mathbf{k})$ are creation and annihilation operators for electrons with momentum $\mathbf{k}$ and spin projection $\hbar/2$; $\hat{b}^+(-\mathbf{k})$, $\hat{b}(-\mathbf{k})$ are creation and annihilation operators for an electron with momentum $-\mathbf{k}$ and spin projection $-\hbar/2$; $w(\mathbf{k}, \mathbf{k}')$ is

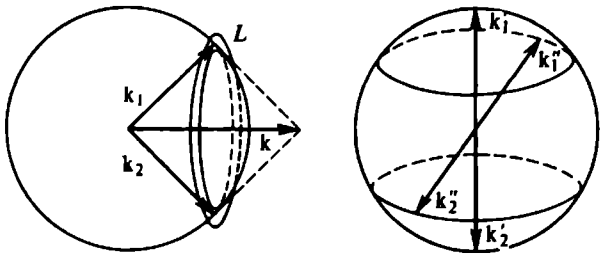


FIG. 93

a function characterizing the interaction between electrons with momenta $\mathbf{k}'$ and $-\mathbf{k}'$. Interaction results in that the momenta of this electron pair become equal to $\mathbf{k}$ and $-\mathbf{k}$, with all the four momenta being confined within the layer of the momentum space close to the Fermi sphere with a thickness $\sim v_D/v_{max}$. In the second term in formula (70.1) summation is performed only over momenta $\mathbf{k}$, $\mathbf{k}'$ lying in this layer. The function $w(\mathbf{k}, \mathbf{k}')$ can be shown [22] to be real-valued and symmetrical with respect to its arguments, $w(\mathbf{k}, \mathbf{k}') = w(\mathbf{k}', \mathbf{k})$. The Hamiltonian (70.1) is known as the *Bardeen-Cooper-Schrieffer* (*BCS*) *Hamiltonian*.

Electron pairs with opposite spin projections and a zero total momentum are referred to as *Cooper pairs*. Cooper discovered that the pairs are capable of forming bound states even at very weak interac-

tions, which stems from the following simple reasoning: in any shallow potential well electron momenta decrease as electrons move apart from each other, since deceleration occurs due to their mutual attraction. At temperatures close to zero, however, the decrease of momentum cannot be infinite. As soon as particle momenta reach the value of k_{max}, further decrease of momentum becomes impossible due to the Pauli exclusion principle, since all "spots" inside the Fermi sphere are occupied by electrons. This means that the further increase in the distance between pair components is impossible, and they form a bound state.

This circumstance is of paramount importance and explains why the theory of superconductivity was created so late (1957). The fact is that inasmuch as the weakest electron interaction changes radically the nature of the energy spectrum, that is changes it from a continuous into a discrete one, the standard methods of the perturbation theory, for instance, the expansion in powers of the interaction function, cannot be applied, and the problem must be solved by other techniques. That is why the discovery that the Cooper pairs are capable of forming bound states (Cooper's phenomenon) served as a clue to the creation of the theory of superconductivity.

Returning to formula (70.1), it should be noted that it is precisely the second term in the Hamiltonian that describes the processes involving the conversion of one Cooper pair $(\mathbf{k}', -\mathbf{k}')$ into the other $(\mathbf{k}, -\mathbf{k})$.

To facilitate calculations, it is convenient to consider formally an electron gas as a system with a variable number of particles. In accordance with the results obtained in Sec. 63 [formula (63.50)], we must then replace in the Gibbs canonical distribution the energy $E(i)$ by the difference $E(i \mid N) - \mu N$, and determine the chemical potential from the normalization condition $N = T\frac{\partial (\ln Q)}{\partial \mu}$. Within the framework of second quantization this means that we must replace the Hamiltonian by the difference $\hat{\mathscr{H}} - \mu\hat{\mathscr{N}}$, where

$$\hat{\mathscr{N}} = \sum_{\mathbf{k}} [\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{b}^+(-\mathbf{k})\,\hat{b}(-\mathbf{k})] \tag{70.2}$$

is the operator of the total number of particles. This difference will be denoted below by $\hat{\mathscr{H}}$ as before and referred to as the Hamiltonian. Therefore, we have

$$\hat{\mathscr{H}} = \sum_{\mathbf{k}} \varepsilon(k)\,[\hat{a}^+(\mathbf{k})\,\hat{a}(\mathbf{k}) + \hat{b}^+(-\mathbf{k})\,\hat{b}(-\mathbf{k})]$$

$$-\frac{1}{V}\sum_{\mathbf{k},\,\mathbf{k}'} w(\mathbf{k},\,\mathbf{k}')\,\hat{a}^+(\mathbf{k})\,\hat{b}^+(-\mathbf{k})\,\hat{b}(-\mathbf{k}')\,\hat{a}(\mathbf{k}'), \tag{70.3}$$

where $\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \mu = \frac{\hbar^2 (k^2 - k_{max}^2)}{2m}$ is the energy for which the Femri surface is the initial level.

Let us introduce the Hermitian conjugate operators $\hat{\Delta}(\mathbf{k})$ and $\hat{\Delta}^+(\mathbf{k})$, determined by the equalities

$$\hat{\Delta}(\mathbf{k}) = \frac{1}{2V} \sum_{\mathbf{k}'} w(\mathbf{k}, \mathbf{k}') \hat{b}(-\mathbf{k}') \hat{a}(\mathbf{k}'),$$
$$\hat{\Delta}^+(\mathbf{k}) = \frac{1}{2V} \sum_{\mathbf{k}'} w(\mathbf{k}, \mathbf{k}') \hat{a}^+(\mathbf{k}') \hat{b}^+(-\mathbf{k}'). \tag{70.4}$$

Due to the hermiticity of the operator in formula (70.3), the expression for it can be rewritten to read

$$\hat{\mathcal{H}}_{int} = -\frac{1}{2V} \sum_{\mathbf{k}, \mathbf{k}'} w(\mathbf{k}, \mathbf{k}') [\hat{a}^+(\mathbf{k}) \hat{b}^+(-\mathbf{k}) \hat{b}(-\mathbf{k}') \hat{a}(\mathbf{k}') + \hat{a}^+(\mathbf{k}') \hat{b}^+(-\mathbf{k}') \hat{b}(-\mathbf{k}) \hat{a}(\mathbf{k})]$$
$$= -\sum_{\mathbf{k}} [\hat{a}^+(\mathbf{k}) \hat{b}^+(-\mathbf{k}) \hat{\Delta}(\mathbf{k}) + \hat{\Delta}^+(\mathbf{k}) \hat{b}(-\mathbf{k}) \hat{a}(\mathbf{k})], \tag{70.5}$$

whence for the total Hamiltonian $\hat{\mathcal{H}}$ we have

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} \varepsilon(k) [\hat{a}^+(\mathbf{k}) \hat{a}(\mathbf{k}) + \hat{b}^+(-\mathbf{k}) \hat{b}(-\mathbf{k})] - \sum_{\mathbf{k}} [\hat{a}^+(\mathbf{k}) \hat{b}^+(-\mathbf{k}) \hat{\Delta}(\mathbf{k}) + \hat{\Delta}^+(\mathbf{k}) \hat{b}(-\mathbf{k}) \hat{a}(\mathbf{k})]. \tag{70.6}$$

It will be shown below that with an accuracy up to the terms of the order of r_0^3/V (r_0 is the electron interaction radius) the quantities $\Lambda(\mathbf{k})$ and $\hat{\Delta}^+(\mathbf{k})$ can be treated not as operators, but as complex conjugate functions of momentum.

The operators $\hat{a}(\mathbf{k})$, $\hat{a}^+(\mathbf{k})$, $\hat{b}(\mathbf{k})$, $\hat{b}^+(\mathbf{k})$ and their Fourier-transforms will be denoted in this section by the same letter. We have

$$\hat{a}(\mathbf{k}) = \frac{1}{\sqrt{V}} \int d^3r\, e^{i\mathbf{k}\mathbf{r}} \hat{a}(\mathbf{r}) = \int d^3r\, \varphi_{\mathbf{k}}(\mathbf{r})\, \hat{a}(\mathbf{r}),$$

where $\varphi_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} e^{i\mathbf{k}\mathbf{r}}$ are the orthonormalized functions introduced in Sec. 68. Let us transform the expression for the operator $\Lambda(\mathbf{k})$ in the following manner:

$$\Lambda(\mathbf{k}) = \frac{1}{2V} \sum_{\mathbf{k}'} w(\mathbf{k}, \mathbf{k}') \hat{b}(-\mathbf{k}') a(\mathbf{k}')$$
$$= \frac{1}{2V} \sum_{\mathbf{k}'} w(\mathbf{k}, \mathbf{k}') \frac{1}{\sqrt{V}} \int d^3r\, e^{-i\mathbf{k}'\mathbf{r}} \hat{b}(\mathbf{r}) \frac{1}{\sqrt{V}} \int d^3r'\, e^{i\mathbf{k}'\mathbf{r}'} \hat{a}(\mathbf{r}')$$
$$= \frac{1}{2V} \int\int d^3r\, d^3r' W(\mathbf{k}, \mathbf{r}' - \mathbf{r}) \hat{b}(\mathbf{r}) \hat{a}(\mathbf{r}'), \tag{70.7}$$

where the notation

$$W(\mathbf{k},\ \mathbf{r}'-\mathbf{r})=\frac{1}{V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\, e^{i(\mathbf{k}',\ \mathbf{r}'-\mathbf{r})},$$

is introduced.

The attention of the reader should be drawn to the fact that the quantity $W(\mathbf{k},\ \mathbf{r}'-\mathbf{r})$ is not a Fourier-transform of the function $w(\mathbf{k},\ \mathbf{k}')$ with respect to the argument $\mathbf{k}'$, but differs from it by the factor $V^{-1/2}$. The so determined function is independent of volume for large V, which becomes particularly clear if we turn in the above formula from the summation over $\mathbf{k}'$ to integration by means of the relation

$$\sum_{\mathbf{k}'} \ldots \to \frac{V}{(2\pi)^3}\int d^3k\ \ldots .$$

Let us also postulate that the function $W(\mathbf{k},\ \mathbf{r}'-\mathbf{r})$, describing the interaction in a coordinate space, has a characteristic radius r_0, i.e. that it decreases rapidly enough at $|\ \mathbf{r}'-\mathbf{r}\ | > r_0$. The squared norm of operator $\hat{\Delta}(\mathbf{k})$ will be shown to remain finite as $V\to\infty$.

Let χ be a wave function of an arbitrary state in an occupation-number space. The squared norm of operator $\hat{\Delta}(\mathbf{k})$ is specified by the formula

$$|\hat{\Delta}(\mathbf{k})\,\chi|^2=\langle\chi|\hat{\Delta}^+(\mathbf{k})\,\hat{\Delta}(\mathbf{k})\,|\chi\rangle.$$

Using relation (70.7) and its Hermitian conjugate, we have

$$|\hat{\Delta}(\mathbf{k})\,\chi|^2=\frac{1}{4V^2}\int\int\int\int d^3r_1\,d^3r_2\,d^3r_3\,d^3r_4 W(\mathbf{k},\ \mathbf{r}_1-\mathbf{r}_2) \times W(\mathbf{k},\ \mathbf{r}_4-\mathbf{r}_3)\,\langle\chi|\hat{a}^+(\mathbf{r}_1)\,\hat{b}^+(\mathbf{r}_2)\,\hat{b}(\mathbf{r}_3)\,\hat{a}(\mathbf{r}_4)|\chi\rangle.$$

In the above integral the interaction functions limit two integrations out of four by the domain $\sim r_0^3$, whereas the two remaining integrations are performed over the volume V. It follows from this that in the limit $V\to\infty$ the quantity $|\ \hat{\Delta}(\mathbf{k})\chi\ |^2$ remains finite.

Let us find now the commutator of operator $\hat{\Delta}(\mathbf{k})$ with $\hat{a}^+(\mathbf{r})$ (it can readily be verified that the commutator of $\hat{\Delta}(\mathbf{k})$ with $\hat{a}(\mathbf{r})$ is identically equal to zero). From formula (70.7) we obtain

$$[\hat{\Delta}(\mathbf{k}),\ \hat{a}^+(\mathbf{r})]=\frac{1}{2V}\int\int d^3r'\,d^3r'' W(\mathbf{k},\ \mathbf{r}''-\mathbf{r}')\,\hat{b}(\mathbf{r}')\,\delta(\mathbf{r}''-\mathbf{r}) = \frac{1}{2V}\int d^3r' W(\mathbf{k},\ \mathbf{r}-\mathbf{r}')\,\hat{b}(\mathbf{r}').$$

From the above formula we find for the squared norm of operator $[\hat{\Delta}(\mathbf{k}),\ \hat{a}^+(\mathbf{r})]$ the following expression:

$$|[\hat{\Delta}(\mathbf{k}),\ \hat{a}^+(\mathbf{r})]|^2 = \frac{1}{4V^2}\int\int d^3r'\,d^3r'' W(\mathbf{k},\ \mathbf{r}-\mathbf{r}')\,W(\mathbf{k},\ \mathbf{r}''-\mathbf{r})\,\langle\chi|\hat{b}^+(\mathbf{r}'')\,\hat{b}(\mathbf{r}')|\chi\rangle.$$

Since the interaction functions limit the two integrations to the domain $\sim r_0^3$, the right-hand side includes the quantity $\sim r_0^6/V^2$ that tends to zero as $V \to \infty$.

Thus, we proved that the quantities $\Delta(\mathbf{k})$ and $\Delta^+(\mathbf{k})$ commute at the limit $V \to \infty$ with operators $\hat{a}(\mathbf{r})$, $\hat{a}^+(\mathbf{r})$, $\hat{b}(\mathbf{r})$, $\hat{b}^+(\mathbf{r})$, and, consequently, with any function of these operators. It follows from this that $\Delta(\mathbf{k})$ and $\Delta^+(\mathbf{k})$ can be considered not as operators, but as complex conjugate numbers. A strict proof of this assertion is based on Schur's lemma in the group theory

If the function of $\Delta(\mathbf{k})$ is assumed to be real-valued*, the Hamiltonian (70.6) can be rewritten to read

$$\mathcal{H} = \sum_{\mathbf{k}} \varepsilon(k) [\hat{a}^+(\mathbf{k}) \hat{a}(\mathbf{k}) + \hat{b}^+(-\mathbf{k}) \hat{b}(-\mathbf{k})] - \sum_{\mathbf{k}} \Delta(\mathbf{k}) [\hat{a}^+(\mathbf{k}) \hat{b}^+(-\mathbf{k}) + \hat{b}(-\mathbf{k}) \hat{a}(\mathbf{k})]. \quad (70.8)$$

In the problem under consideration (as was already mentioned) the interaction of Cooper electron pairs cannot be ignored, even at a low interaction potential. In fact, as was demonstrated, even the weakest attraction leads to the appearance of bound states of Cooper pairs. Calculation results, formula (70.31), also demonstrate that one cannot neglect the interaction. It follows from this that the system of operators $\hat{a}(\mathbf{k})$, $\hat{a}^+(\mathbf{k})$, $\hat{b}(\mathbf{k})$, $\hat{b}^+(\mathbf{k})$ cannot serve as an initial approximation for the perturbation theory.

Let us introduce quasi-particles that are superpositions of a particle having momentum $\mathbf{k}$ and spin projection $\hbar/2$, and of a particle with momentum $-\mathbf{k}$ and spin projection $-\hbar/2$. For this purpose we carry out the Bogoliubov canonical transformation for Fermi operators [cf. Eq. (69.7) for Bose operators]:

$$\begin{aligned} \hat{a}(\mathbf{k}) &= \hat{\xi}(\mathbf{k}) \cos\varphi(\mathbf{k}) + \hat{\eta}^+(-\mathbf{k}) \sin\varphi(\mathbf{k}), \\ \hat{b}(-\mathbf{k}) &= -\hat{\xi}^+(\mathbf{k}) \sin\varphi(\mathbf{k}) + \hat{\eta}(-\mathbf{k}) \cos\varphi(\mathbf{k}), \\ \hat{a}^+(\mathbf{k}) &= \hat{\xi}^+(\mathbf{k}) \cos\varphi(\mathbf{k}) + \hat{\eta}(-\mathbf{k}) \sin\varphi(\mathbf{k}), \\ \hat{b}^+(-\mathbf{k}) &= -\hat{\xi}(\mathbf{k}) \sin\varphi(\mathbf{k}) + \hat{\eta}^+(-\mathbf{k}) \cos\varphi(\mathbf{k}), \end{aligned} \quad (70.9)$$

where $\varphi(\mathbf{k})$ is the as yet unknown function of momentum $\mathbf{k}$. It can be easily verified that transformation (70.9) is a canonical one and that its anticommutators remain unchanged. For this reason operators $\hat{\xi}(\mathbf{k})$, $\hat{\xi}^+(\mathbf{k})$, $\hat{\eta}(\mathbf{k})$, $\hat{\eta}^+(\mathbf{k})$ satisfy the same commutation

* The reader is to convince himself that $\Delta(\mathbf{k})$ can be chosen real-valued on the basis of Eq. (70.20).

relations as operators $\hat{a}(\mathbf{k})$, $\hat{a}^+(\mathbf{k})$, $\hat{b}(\mathbf{k})$, $\hat{b}^+(\mathbf{k})$:

$$\hat{\xi}(\mathbf{k})\,\hat{\xi}(\mathbf{k}') + \hat{\xi}(\mathbf{k}')\,\hat{\xi}(\mathbf{k}) = 0,$$
$$\hat{\xi}^+(\mathbf{k})\,\hat{\xi}^+(\mathbf{k}') + \hat{\xi}^+(\mathbf{k}')\,\hat{\xi}^+(\mathbf{k}) = 0, \qquad (70.10)$$
$$\hat{\xi}(\mathbf{k})\,\hat{\xi}^+(\mathbf{k}') + \hat{\xi}^+(\mathbf{k}')\,\hat{\xi}(\mathbf{k}) = \delta_{\mathbf{k},\mathbf{k}'}.$$

The same relations are true for operators $\hat{\eta}(\mathbf{k})$, $\hat{\eta}^+(\mathbf{k})$. Operators $\hat{\xi}(\mathbf{k})$, $\hat{\xi}^+(\mathbf{k})$ anticommute with operators $\hat{\eta}(\mathbf{k})$, $\hat{\eta}^+(\mathbf{k})$, allowing us to consider $\hat{\xi}^+(\mathbf{k})$, $\hat{\eta}^+(\mathbf{k})$ as creation operators, and $\hat{\xi}(\mathbf{k})$, $\hat{\eta}(\mathbf{k})$ as annihilation operators for quasi-particles of two kinds, ξ-particles and η-particles, with these quasi-particles being, as can be seen from formula (70.9), linear superpositions of particles with antiparallel spin and a total momentum equal to zero.

Substituting formulae (70.9) into (70.8), we find the Hamiltonian in new variables:

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} \{\varepsilon(k)[1-\cos 2\varphi(\mathbf{k})] - \Delta(\mathbf{k})\sin 2\varphi(\mathbf{k})\}$$
$$+ \sum_{\mathbf{k}} [\varepsilon(k)\cos 2\varphi(\mathbf{k}) + \Delta(\mathbf{k})\sin 2\varphi(\mathbf{k})][\hat{\xi}^+(\mathbf{k})\,\hat{\xi}(\mathbf{k}) + \hat{\eta}^+(-\mathbf{k})\,\hat{\eta}(-\mathbf{k})]$$
$$+ \sum [\varepsilon(k)\sin 2\varphi(\mathbf{k}) - \Delta(\mathbf{k})\cos 2\varphi(\mathbf{k})][\hat{\xi}^+(\mathbf{k})\,\hat{\eta}^+(-\mathbf{k}) + \hat{\eta}(-\mathbf{k})\,\hat{\xi}(\mathbf{k})]. \qquad (70.11)$$

Let us now select parameter $\varphi(\mathbf{k})$ so that the last term becomes zero. In the occupation-number representation of ξ- and η-quasi particles the Hamiltonian becomes diagonal; then the terms describing the processes of simultaneous creation and annihilation of ξ and η quasi-particles vanish and the diagonal elements provide the system's energy spectrum.

The physical meaning of this is that we have turned from the consideration of a real gas of interacting electrons to an ideal gas of non-interacting quasi-particles.

The diagonality condition for Hamiltonian (70.11) is

$$\tan 2\varphi(\mathbf{k}) = \frac{\Delta(\mathbf{k})}{\varepsilon(k)}, \qquad (70.12)$$

and we select the following values of $\sin 2\varphi(\mathbf{k})$ and $\cos 2\varphi(\mathbf{k})$ satisfying condition (70.12):

$$\sin 2\varphi(\mathbf{k}) = \frac{\Delta(\mathbf{k})}{\omega(\mathbf{k})}, \quad \cos 2\varphi(\mathbf{k}) = \frac{\varepsilon(k)}{\omega(\mathbf{k})}, \qquad (70.13)$$

where

$$\omega(\mathbf{k}) = \sqrt{\varepsilon^2(k) + \Delta^2(\mathbf{k})}. \qquad (70.14)$$

Substituting Eqs. (70.13) and (70.14) into Eq. (70.11), we get

$$\hat{\mathscr{H}} = \sum_{\mathbf{k}} [\varepsilon(k) - \omega(\mathbf{k})] + \sum_{\mathbf{k}} \omega(\mathbf{k}) [\hat{\xi}^+(\mathbf{k}) \hat{\xi}(\mathbf{k}) + \hat{\eta}^+(-\mathbf{k}) \hat{\eta}(-\mathbf{k})]. \tag{70.15}$$

The first term in formula (70.15) is independent of the number of quasi-particles and represents the ground-state energy, and the second term is the sum of energies of quasi-particles [$\omega(\mathbf{k})$ is the energy of one quasi-particle].

To elaborate the thermodynamics of a superconductor, it is necessary to find the average value of operator $\hat{\mathscr{H}}$ for a state at a difinite temperature T, performing the averaging in two stages. First, we find the quantum-mechanical average (the diagonal matrix element) of $\hat{\mathscr{H}}$ over a state with an arbitrarily fixed number of quasi-particles n_ξ and n_η. Then, we average this matrix element over the Gibbs ensemble with temperature T. This leads to the replacement of the arbitrary quasi-particle numbers n_ξ and n_η by their most probable values at the given temperature $n_\xi(T)$ and $n_\eta(T)$. Since the quasi-particles are non-interacting fermions and their number is not fixed in contrast to the number of real particles, electrons, then the most probable numbers $n_\xi(T)$ and $n_\eta(T)$ are determined by the Fermi-Dirac distribution formulae with a zero chemical potential (the same way the numbers of photons and phonons are determined by the Bose-Einstein formulae with $\mu = 0$).

It should be noted that the two-stage averaging procedure is applied not only to the numbers of quasi-particles $\hat{\xi}^+(\mathbf{k})\,\hat{\xi}(\mathbf{k})$, $\eta^+(\mathbf{k})\,\hat{\eta}(\mathbf{k})$, but also to the quantity $\Delta(\mathbf{k})$, inasmuch as operators $\hat{a}(\mathbf{k})$ and $\hat{b}(\mathbf{k})$ are pertinent in its determination. In consequence, the average value of $\Delta(\mathbf{k})$ will depend on temperature, and we shall denote it by $\Delta(\mathbf{k}, T)$. Thus, the averaging procedure results in both the energy of a quasi-particle $\omega(\mathbf{k})$ and Bogoliubov's transformation parameter $\varphi(\mathbf{k})$ becoming functions of temperature. We denote these average values by $\omega(\mathbf{k}, T)$ and $\varphi(\mathbf{k}, T)$, expressed by

$$\omega(\mathbf{k}, T) = \sqrt{\varepsilon^2(k) + \Delta^2(\mathbf{k}, T)}, \tag{70.16}$$

$$\sin 2\varphi(\mathbf{k}, T) = \frac{\Delta(\mathbf{k}, T)}{\omega(\mathbf{k}, T)}. \tag{70.17}$$

In accordance with the above, the average numbers of quasi-particles are found to be expressed by

$$n_\xi(T) = n_\eta(T) = n(\mathbf{k}, T) = [e^{\omega(\mathbf{k}, T)/T} + 1]^{-1}. \tag{70.18}$$

Let us find the equation governing the function $\Delta(\mathbf{k}, T)$. Replacing in formula (70.4) the operators $\hat{b}(-\mathbf{k})$, $\hat{a}(\mathbf{k})$ according to (70.9),

we obtain

$$\hat{\Delta}(\mathbf{k}) = \frac{1}{2V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\,[-\hat{\xi}^{+}(\mathbf{k}')\sin\varphi(\mathbf{k}') + \hat{\eta}(-\mathbf{k}')\cos\varphi(\mathbf{k}')]$$

$$\times\,[\hat{\xi}(\mathbf{k}')\cos\varphi(\mathbf{k}') + \hat{\eta}^{+}(-\mathbf{k}')\sin\varphi(\mathbf{k}')]. \quad (70.19)$$

Since $\hat{\Delta}(\mathbf{k})$ is a c-number (to terms of the order of r_0^3/V), it coincides with its diagonal matrix element. Leaving on the right-hand side of formula (70.19) only the diagonal operators $\hat{\xi}^{+}(\mathbf{k}')\ \hat{\xi}(\mathbf{k}')$ and $\hat{\eta}(-\mathbf{k}')\ \hat{\eta}^{+}(-\mathbf{k}')$ and replacing them by their eigenvalues n_ξ and $1 - n_\eta$, we find

$$\Delta(\mathbf{k}) = \frac{1}{4V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\sin 2\varphi(\mathbf{k}')\,(1 - n_\xi - n_\eta)$$

$$= \frac{1}{4V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\frac{\Delta(\mathbf{k}')}{\omega(\mathbf{k}')}(1 - n_\xi - n_\eta).$$

Averaging out the above equation over the state at temperature T and using formula (70.18), we find

$$\Delta(\mathbf{k},\ T) = \frac{1}{4V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\frac{\Delta(\mathbf{k}',\ T)}{\omega(\mathbf{k}',\ T)}\tanh\frac{\omega(\mathbf{k}',\ T)}{2T}, \quad (70.20)$$

or

$$\Delta(\mathbf{k},\ T)$$

$$= \frac{1}{4V}\sum_{\mathbf{k}'} w(\mathbf{k},\ \mathbf{k}')\frac{\Delta(\mathbf{k}',\ T)}{\sqrt{\varepsilon^2(k') + \Delta^2(\mathbf{k}',\ T)}}\tanh\frac{\sqrt{\varepsilon^2(k') + \Delta^2(\mathbf{k}',\ T)}}{2T}. \quad (70.21)$$

We obtained an integral equation for $\Delta(\mathbf{k},\ T)$, from which it follows, in particular, that a function $\Delta(\mathbf{k},\ T)$ can be taken real, as was assumed in deriving formula (70.8). Equation (70.21) has a trivial solution $\Delta(\mathbf{k},\ T) = 0$. At sufficiently strong electron-phonon interaction and sufficiently low temperatures, however, the equation also has a non-trivial solution $\Delta(\mathbf{k},\ T) \neq 0$. To find this non-trivial solution, let us simplify the model further and replace the function $w(\mathbf{k},\ \mathbf{k}')$ in the layer in which it is assumed to differ from zero by its averaged value g. As is seen from formula (70.4), the quantity Δ is then independent of momentum. Then, after cancelling out the factor $\Delta \neq 0$, Eq. (70.21) reduces to

$$1 = \frac{g}{4V}\sum_{\mathbf{k}} \frac{\tanh\dfrac{\sqrt{\varepsilon^2(k) + \Delta^2(T)}}{2T}}{\sqrt{\varepsilon^2(k) + \Delta^2(T)}}, \quad (70.22)$$

or at $T = 0$

$$1 = \frac{g}{4V} \sum_{\mathbf{k}} \frac{1}{\sqrt{\varepsilon^2(k) + \Delta^2(0)}}. \tag{70.23}$$

The condition for Eq. (70.23) to have a non-zero solution has the form

$$\frac{g}{4V} \sum_{\mathbf{k}} \frac{1}{|\varepsilon(k)|} > 1, \tag{70.24}$$

i.e. a sufficiently strong electron-phonon interaction is required.

Before solving Eq. (70.23), let us elucidate the physical meaning of the quantity $\Delta(T)$, which is of paramount importance in the theory of superconductivity. Let us return to formula (70.15) and average the Hamiltonian over the Gibbs ensemble at temperature T. We have

$$\overline{E}(T) = \sum_{\mathbf{k}} [\varepsilon(k) - \omega(k, T)] + \sum_{\mathbf{k}} \frac{2\omega(k, T)}{e^{\omega(k, T)/T} + 1}$$

$$= \sum_{\mathbf{k}} [\varepsilon(k) - \sqrt{\varepsilon^2(k) + \Delta^2(T)}] + \sum_{\mathbf{k}} \frac{2\sqrt{\varepsilon^2(k) + \Delta^2(T)}}{\exp\left[\frac{[\varepsilon^2(k) + \Delta^2(T)]^{1/2}}{T}\right] + 1}. \tag{70.25}$$

In particular, at $T = 0$ the mean energy is equal to the energy of the ground state, in which there are no quasi-particles:

$$\overline{E}(0) = \sum_{\mathbf{k}} [\varepsilon(k) - \sqrt{\varepsilon^2(k) + \Delta^2(0)}]. \tag{70.26}$$

It is clear that the non-trivial solution $\Delta(0) \neq 0$ corresponds to a lower ground-state energy than the zero solution $\Delta(0) = 0$. In the latter case, we have

$$\overline{E}(0) = \sum_{\mathbf{k}} [\varepsilon(k) - |\varepsilon(k)|] = 2 \sum_{\varepsilon(k)<0} \varepsilon(k),$$

which corresponds to the state in which all electron levels inside the Fermi sphere are occupied, and all levels outside the Fermi sphere are free (it should be recalled that $\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \mu$ is the electron energy for which the Fermi boundary is the reference). At $\Delta(0) \neq 0$

$$\overline{E}(0) < 2 \sum_{\varepsilon(k)<0} \varepsilon(k).$$

Thus, at $T = 0$ the solution with $\Delta(0) \neq 0$ is thermodynamically expedient. It is clear that this situation is also true for sufficiently low temperatures.

The solution $\Delta(0) \neq 0$ will be shown now to correspond to the superconductive state of an electron gas. The energy of a quasi-particle, $\omega(k, 0) = \sqrt{\varepsilon^2(k) + \Delta^2(0)}$, diminishes as the Fermi surface is approached and acquires its minimum value $\Delta(0)$ on the Fermi surface. Thus, we have $\omega(k, 0) \geqslant \Delta(0)$, meaning that the first excited state of a system is separated from its ground state by the forbidden energy region—the energy gap. Since the quasi-particles ξ and η have spin $\hbar/2$, they can appear only in pairs, in accordance

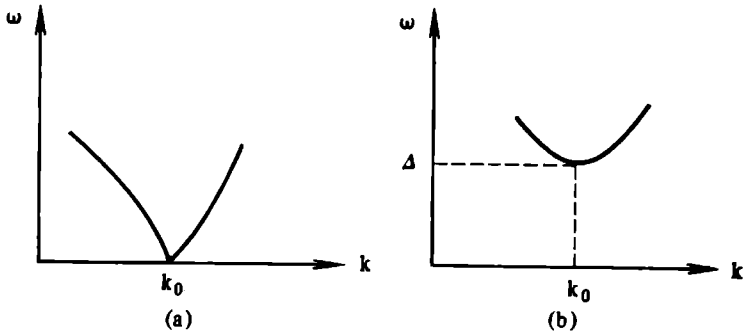


FIG. 94

with the spin conservation law. Hence, the energy gap is equal to $2\Delta(0)$ at $T = 0$ and at an arbitrary temperature T, to $2\Delta(T)$. Since in the state with $\Delta \neq 0$ the minimum value of $\omega(k, T)/k \geqslant \Delta(T)/k$ differs from zero, the system [see condition (69.15)] must possess superfluidity. For an electron gas in a conductor this property manifests itself in the form of *superconductivity*.

In fact, if an ordered motion of electrons (current), having a mean momentum P, commences in a metal, the associated energy increment is determined by the quantity $\mathbf{P}\frac{\partial \varepsilon}{\partial \mathbf{P}} = \frac{\hbar k \mathbf{P}}{m}$. Upon decay of the state with the current the energy diminishes by the same value. However, for that state to decay energy of an order of magnitude of 2Δ must be spent. This becomes very clear when the process is considered in a reference frame in respect to which no ordered motion exists. For such motion to begin, quasi-particles must be created, involving an energy expenditure of 2Δ. Thus, if the inequality $\frac{\hbar k \mathbf{P}}{m} < \Delta$ is observed, the state with the current is stable. In other words, there is no resistance to current flow at sufficiently small P or sufficiently small current densities.

Let us illustrate the difference between the normal $\Delta = 0$ [Fig. 94 (*a*)] and the superconducting $\Delta \neq 0$ [Fig. 94 (*b*)] states, plot-

ting the energy of a quasi-particle as a function of momentum. At $\Delta = 0$ we have

$$\omega(k) = \varepsilon(k) = \begin{cases} \frac{\hbar^2 k^2}{2m} - \mu & \text{at } k \geqslant k_{\max}, \\ \mu - \frac{\hbar^2 k^2}{2m} & \text{at } k \leqslant k_{\max}. \end{cases}$$

At $\Delta \neq 0$

$$\omega(k) = \sqrt{\left(\frac{\hbar^2 k^2}{2m} - \mu\right)^2 + \Delta^2(0)}.$$

Let us return now to Eq. (70.23) for the energy gap at $T = 0$. Let us integrate over $\mathbf{k}$ on the right-hand side of the equation; allowing for the fact that the integrand in (70.23) depends only on k, and replacing $\sum_{\mathbf{k}} \ldots$ by $\frac{V}{2\pi^2}\int dk\, k^2 \ldots$, we integrate over the thin spherical layer in the vicinity of the Fermi surface, about $\nu_{\max}/v_{\max}$ thick, obtaining

$$1 = \frac{g}{2\pi^2}\int_{k_{\max}-\tau}^{k_{\max}+\tau} \frac{k^2\, dk}{\sqrt{\varepsilon^2(k) + \Delta^2(0)}}, \tag{70.27}$$

where $\tau = B\nu_{\max}/v_{\max}$, and B is a numerical factor. Since $\tau \ll k_{\max}$, the slowly changing factor k^2 in the integral on the right-hand side of formula (70.27) can be replaced by $k_{\max}^2$ and we can transform $\varepsilon(k)$ in the following manner:

$$\varepsilon(k) = \frac{\hbar^2(k^2 - k_{\max}^2)}{2m} \approx \hbar v_{\max}(k - k_{\max}).$$

Formula (70.27) then reduces to

$$1 = \frac{g}{\Lambda}\int_0^{\hbar v_{\max}\tau} \frac{d\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2(0)}}, \quad \Lambda = \frac{4\pi^2\hbar^3}{m p_{\max}}. \tag{70.28}$$

Introducing a new integration constant φ by the formula $\varepsilon = \Delta(0)\sinh\varphi$, we obtain

$$1 = \frac{g}{\Lambda}\operatorname{arsinh}\left(\frac{\hbar v_{\max}\tau}{\Delta(0)}\right). \tag{70.29}$$

It has been shown by experiment that $\frac{\Delta(0)}{\hbar v_{\max}\tau} \sim \frac{\Delta(0)}{\hbar\nu_{\max}} \ll 1$, which is why formula (70.29) acquires the form

$$1 = \frac{g}{\Lambda}\ln\left(\frac{2\hbar v_{\max}\tau}{\Delta(0)}\right), \tag{70.30}$$

whore we obtain

$$\Delta(0) = 2\hbar v_{\max}\tau e^{-\Lambda/g} = 2B\hbar\nu_{\max}e^{-\Lambda/g}. \tag{70.31}$$

Expression (70.31) indicates once more that the perturbation theory is invalid: the function $e^{-\Lambda/g}$ has at $g = 0$ essential singularity in the vicinity of which the function cannot be expanded into a series in g.

The reader's attention should be drawn to the fact that for superconductivity to appear (70.24) there must be a sufficiently strong electron-phonon interaction. But it is precisely this interaction that gives rise to the resistance to electric current flow at temperatures differing from zero. It follows from this that metals, being good conductors at high temperatures, should not pass to the superconducting state at low temperatures, and vice versa. This assertion has been well substantiated by experiments—copper, silver, and gold do not pass to the superconducting state down to the lowest temperatures presently attainable. On the contrary, such poor conductors as lead, mercury, niobium move to the superconducting state at the highest temperatures.

It should also be noted that the idea of superconductivity, being the result of the appearance of Cooper pairs, must be taken as rather conditional. The idea of coupled pairs is sufficiently realistic in the momentum space. The correlation of the states of the particles of a pair leads to the high probability of their common state with a total momentum equal to zero. But the validity of this concept is rather restricted in the coordinate space.

Indeed, let us estimate the average dimension of a pair, i.e. the distance between the pair components. The order of magnitude of the momentum spread is $\frac{\Delta(0)}{v_{\max}}$, corresponding to the energy spread in the correlated pair, $\sim\Delta(0)$. Hence, the distance between pair components, l, is of the order of $l \sim \frac{\hbar}{\delta p} \sim \frac{\hbar v_{\max}}{\Delta(0)}$, i.e. according to formula (70.31), $l \sim \left(\frac{v_{\max}}{v_{\max}}\right) e^{\Lambda/g}$. Using formulae (53.6) and (57.5),

$$v_{\max} = u\left(\frac{3N}{4\pi V}\right)^{1/3} \quad \text{and} \quad v_{\max} = \frac{p_{\max}}{m} = \frac{2\pi\hbar}{m_1}\left(\frac{3N}{8\pi V}\right)^{1/3},$$

we find the estimate to be

$$l \sim \left(\frac{V}{N}\right)^{1/3} \frac{v_{\max}}{u} e^{\Lambda/g}.$$

Since the ratio of the Fermi velocity $v_{\max}$ to the sound velocity and the exponential $e^{\Lambda/g}$ are large compared to unity, the "radius" of a pair, l, is large compared to the interelectron distance $(V/N)^{1/3}$. This is indicative of the fact that the idea of coupled Cooper pair in the coordinate space is particularly conditional.

Let us now solve the equation for the energy gap at $T \neq 0$. Transforming Eq. (70.22) in the same manner as Eq. (70.23), we obtain

Instead of Eq. (70.29),

$$1=\frac{g}{\Lambda}\int_0^b d\varphi \tanh\left[\frac{\Delta(T)}{2T}\cosh\varphi\right],\quad \text{where } b=\operatorname{arsinh}\left(\frac{\hbar\nu_{\max}\tau}{\Delta(T)}\right). \tag{70.32}$$

We transform this equation as follows:

$$1=\frac{g}{\Lambda}\left\{\int_0^b d\varphi\left[\tanh\left(\frac{\Delta(T)}{2T}\cosh\varphi\right)-1\right]+\operatorname{arsinh}\left(\frac{\hbar\nu_{\max}\tau}{\Delta(T)}\right)\right\}$$

$$\approx\frac{g}{\Lambda}\left\{-2\int_0^\infty\frac{d\varphi}{e^{\frac{\Delta(T)}{T}\cosh\varphi}+1}+\ln\left(\frac{\hbar\nu_{\max}\tau}{\Delta(T)}\right)\right\}. \tag{70.33}$$

The upper limit in the convergent integral was replaced by ∞ and use was made of the inequality $\frac{\hbar\nu_{\max}\tau}{\Delta(T)}\gg 1$.

Hence, using formula (70.30), we obtain the equation relating $\Lambda(T)$ and $\Delta(0)$:

$$\ln\frac{\Delta(0)}{\Delta(T)}=2\int_0^\infty\frac{d\varphi}{e^{\frac{\Delta(T)}{T}\cosh\varphi}+1}. \tag{70.34}$$

The integral on the right-hand side of Eq. (70.34) can be evaluated with the aid of the expansion

$$\left(e^{\frac{\Delta(T)}{T}\cosh\varphi}+1\right)^{-1}=\sum_{m=1}^{\infty}(-1)^{m-1}e^{-\frac{m\Delta(T)}{T}\cosh\varphi} \tag{70.35}$$

and the formula

$$\int_0^\infty d\varphi\cosh(\alpha\varphi)e^{-\beta\cosh\varphi}=K_\alpha(\beta), \tag{70.36}$$

where $K_\alpha(\beta)$ is the Bessel function of an imaginary argument (see, for instance, [23], formula (3.547.4)). Hence,

$$\ln\frac{\Delta(0)}{\Delta(T)}=2\sum_{m=1}^{\infty}(-1)^{m-1}K_0\left(\frac{m\Delta(T)}{T}\right). \tag{70.37}$$

At low temperatures we can limit ourselves to the first term of the expansion and use the representation of the function $K_0(z)\propto\sqrt{\frac{\pi}{2z}}e^{-z}$. Thus, accurate to infinitesimals of the order of $\frac{\Delta(0)-\Delta(T)}{T}$, we obtain

$$\Delta(T)=\Delta(0)-\sqrt{2\pi T\Delta(0)}\,e^{-\Delta(0)/T}. \tag{70.38}$$

The quantity $\Delta(T)$ decreases with rising temperature and vanishes at T_{cr}—a phase transition from the superconducting to the normal state takes place.

For the series in (70.37) at small values of Δ/T it is convenient to use the formula:

$$\sum_{m=1}^{\infty}(-1)^m K_0(mx)=\frac{1}{2}\left(C+\ln\frac{x}{\pi}\right)+\pi\sum_{l=1}^{\infty}\left[\frac{1}{\sqrt{x^2+(2l-1)^2\pi^2}}-\frac{1}{(2l-1)\pi}\right],$$

where $C=\ln\gamma=0.577$ is Euler's constant (see, for instance, [23], formula (8.526.2)).

Substituting this into formula (70.37), we get

$$\ln\frac{\Delta(0)}{\Delta(T)}=\ln\frac{\pi T}{\gamma\Delta(T)}+2\pi\sum_{l=1}^{\infty}\left[\frac{1}{(2l-1)\pi}-\frac{1}{\sqrt{(2l-1)^2\pi^2+\Delta^2(T)/T^2}}\right]. \tag{70.39}$$

Assuming $\Delta(T)\to 0$, we find the relation between $\Delta(0)$ and the transition temperature:

$$\frac{\Delta(0)}{T_{cr}}=\frac{\pi}{\gamma}=1.76. \tag{70.40}$$

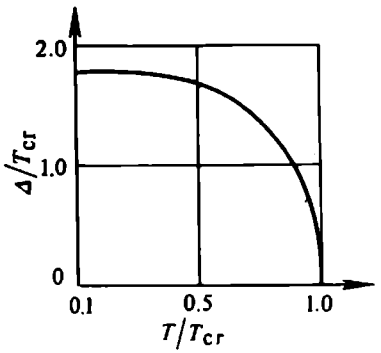


FIG. 95

In the next approximation in $\frac{T_{cr}-T}{T_{cr}}$ we find, from formula (70.39),

$$\frac{\Delta(T)}{T_{cr}}=\frac{2\sqrt{2\pi}}{\sqrt{7\zeta(3)}}\sqrt{\frac{T_{cr}-T}{T_{cr}}}=3.06\sqrt{\frac{T_{cr}-T}{T_{cr}}}. \tag{70.41}$$

Equation (70.39) can be used to find the ratio $\Delta(T)/T_{cr}$ for the intermediate (between 0 and T_{cr}) temperature interval (Fig. 95).

According to formulae (70.40) and (70.31), $\Delta(0)$ and the transition temperature T_{cr} are proportional to the Debye frequency ν_{max} and, consequently, inversely proportional to $\sqrt{M}$ (M is the atomic mass), $T_{cr}\propto M^{-1/2}$. This phenomenon is called the *isotope effect* and is corroborated qualitatively by experimental studies.

Let us find the heat capacity of a superconductor. According to the formula for the entropy of a gas of quasi-particles [see formula (35.8)],

$$S = -\sum_{\mathbf{k}} [n_\xi \ln n_\xi + (1-n_\xi)\ln(1-n_\xi) + n_\eta \ln n_\eta + (1-n_\eta)\ln(1-n_\eta)] = -2\sum_{\mathbf{k}} \{n(\mathbf{k}, T)\ln n(\mathbf{k}, T) + [1-n(\mathbf{k}, T)]\ln[1-n(\mathbf{k}, T)]\},$$

we find that the heat capacity

$$C_s = T\frac{\partial S}{\partial T} = 2T\sum_{\mathbf{k}} \ln\left[\frac{1-n(\mathbf{k}, T)}{n(\mathbf{k}, T)}\right]\frac{dn(\mathbf{k}, T)}{dT}. \qquad (70.42)$$

For the sake of brevity the subscript indicating the constancy of volume is omitted at heat capacity C and the subscript "s" is used, indicating the superconducting state.

Substituting the equilibrium value of $n(\mathbf{k}, T)$ from Eq. (70.18) and integrating over ε, we obtain

$$C_s = \frac{2V}{\Lambda T^2}\int_0^{\hbar v_{\max}\varkappa} \frac{d\varepsilon}{\cosh^2[\omega(k, T)/2T]}\left[\omega^2(k, T) - \frac{T}{2}\frac{d\Delta^2(T)}{dT}\right]. \qquad (70.43)$$

Let us first consider the behaviour of heat capacity in the low-temperature region $T \ll \Delta(0)$. Then, the second term in the brackets in integral (70.43) can be ignored compared with the first term, and replacing $\cosh(\omega/2T)$ by the expression $\frac{1}{2}e^{\omega/2T}$ and extending the integration to ∞, we obtain

$$C_s = \frac{8V}{\Lambda T^2}\int_0^{\infty} \omega^2 e^{-\omega(\mathbf{k}, T)/T} d\varepsilon. \qquad (70.44)$$

It should also be noted that in integral (70.44) a substantial contribution is made only by small values $\varepsilon \ll \Delta(0)$. It is, therefore, possible to replace the factor ω^2 by $\Delta^2(0)$ and to use in the exponent the expansion $\omega = \Delta(0) + \varepsilon^2/2\Delta(0)$. Then

$$C_s = \frac{8V\Delta^2(0)}{\Lambda T^2}\int_0^{\infty} d\varepsilon e^{-\varepsilon^2/2\Delta(0)T} e^{-\Delta(0)/T}$$

and, evaluating the integral, we obtain

$$C_s = \frac{4\sqrt{2\pi}V\Delta^{5/2}(0)}{\Lambda T^{3/2}} e^{-\Delta(0)/T}.$$

Relating heat capacity C_s to that of an electron gas in the normal state at $T = T_{cr}$, we have, according to formula (57.17),

$$C_n(T_{cr}) = \frac{\pi^2 N m}{p^2_{max}} T_{cr}$$

and, using formula (57.5), $p_{max} = \left(\frac{3N}{8\pi V}\right)^{1/3} h$, expression (70.28) for Λ, and relationship (70.40), we finally obtain

$$\frac{C_s(T)}{C_n(T_{cr})} = \frac{3}{\gamma}\sqrt{\frac{2}{\pi}}\left[\frac{\Delta(0)}{T}\right]^{3/2} e^{-\Delta(0)/T}. \qquad (70.45)$$

The exponential decrease in the heat capacity of a superconductor as $T \to 0$ is well corroborated by experiments and it is indicative of the fact that the idea of the existence of an energy gap in the quasi-particle energy spectrum, hampering the transition of quasi-particles to excited states, is correct.

Let us consider now the interval of temperatures close to T_{cr}, with the aim of calculating the discontinuity jump experienced by

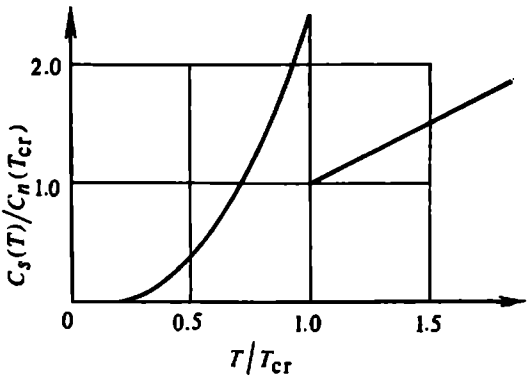


FIG. 96

the heat capacity in passing from the normal to the superconducting state. Since in the normal state $\Delta \equiv 0$, $\omega \equiv \varepsilon$, and in the superconducting state $\Delta = 0$, $\omega = \varepsilon$ at $T = T_{cr}$, the discontinuity jump in heat capacity is determined by the second term in integral (70.43), and we have

$$C_s - C_n = -\frac{2V}{\Lambda}\frac{d[\Delta^2(T)]}{dT}\bigg|_{T=T_{cr}}. \qquad (70.46)$$

Use was made of the fact that at $T \approx T_{cr}$

$$\int_0^{\hbar v_{max}/T} \frac{d\varepsilon}{\cosh^2[\omega(k, T)/2T]} \approx \int_0^{\infty} \frac{d\varepsilon}{\cosh^2(\varepsilon/2T)} = 2T.$$

Differentiating the expression for $\Delta^2(T)$, yielding from formula (70.41), substituting it into formula (70.46) and relating the discontinuity jump $C_s - C_n$ to $C_n(T_{cr})$, we obtain

$$\frac{C_s - C_n}{C_n}\Big|_{T=T_{cr}} = \frac{12}{7\zeta(3)} = 1.43. \tag{70.47}$$

The dependence of C_s/C_n on temperature is shown graphically in Fig. 96. The universal formulae (70.38), (70.40), (70.41), (70.45) and (70.47) are true in a weak-bond approximation, $\frac{\Delta(0)}{\hbar\nu_{max}} \ll 1$, and agree qualitatively with experimental data for "weak" superconductors.

CHAPTER VII

THEORY OF FLUCTUATIONS

The difference between a statistical and purely thermodynamic interpretation manifests itself most vividly in the existence of fluctuation processes. The observation of fluctuations, i.e. the spontaneous passing from the most probable to less probable states, is indicative of the insufficient generality of the purely thermodynamic notion of equilibrium state and serves at the same time as a corroboration of the atomic and molecular theory.

In a macroscopic system only small fluctuations are noticeably probable. However, larger-scale fluctuations are also possible in a system with a small number of degrees of freedom, due to which fact the application of thermodynamic laws becomes totally incorrect.

It should also be noted that fluctuations in measuring instruments give rise to an absolute measurement error, independent of the degree of instrument perfection, which limits the measurement accuracy of even high-class instruments.

71. Fluctuations in Energy, Volume and Number of Particles

For most practical problems it is sufficient to characterize different fluctuation processes with the aid of the so-called root-mean-square fluctuation (*dispersion*) of some physical quantity L, determined by the formula

$$(\mathrm{D}L)^2 = \overline{(L-\overline{L})^2} = \overline{L^2} - (\overline{L})^2, \tag{71.1}$$

and by the relative fluctuation

$$\delta L = \frac{\mathrm{D}L}{L}, \tag{71.2}$$

Let us calculate the fluctuation in energy, volume and number of particles in T-V-N, T-V-μ and T-P-N systems.

For a T-V-N system we have

$$\overline{E} = -\frac{\partial}{\partial \beta}[\ln Z(\beta)]$$

and

$$\overline{E^2} = \frac{1}{Z}\sum_i E_i^2 e^{-\beta E_i} g(i) = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \tag{71.3}$$

whence we find

$$(\mathrm{D}E)^2 = \frac{\partial^2}{\partial \beta^2}[\ln Z(\beta)] = -\frac{\partial \overline{E}}{\partial \beta}. \tag{71.4}$$

Passing to the variable $T = \beta^{-1}$, we obtain

$$(\mathrm{D}E) = T^2 \frac{\partial \overline{E}}{\partial T} = T^2 C_V. \tag{71.5}$$

Let us examine some particular cases of formula (71.5).

For an ideal gas $\overline{E} = lNT/2$, $C_V = lN/2$, consequently

$$\mathrm{D}E = T \sqrt{\frac{lN}{2}}, \tag{71.6}$$

so that the relative fluctuation δE is equal to

$$\delta E = \frac{\mathrm{D}E}{\overline{E}} = \sqrt{\frac{2}{lN}} \tag{71.7}$$

and is very small for macroscopic systems.

For a crystal at $T \ll \theta$ (see Sec. 38) we have

$$\overline{E} = \frac{\pi^4 NT^4}{5\theta^3}, \quad C_V = \frac{\pi^4 NT^3}{5\theta^3}, \tag{71.8}$$

whence the dispersion and relative fluctuations are expressed by

$$\mathrm{D}E = 2\pi^2 \left(\frac{N}{5\theta^3}\right)^{1/2} T^{5/2}, \tag{71.9}$$

$$\delta E = \frac{10}{5^{1/2}\pi^2} \left(\frac{\theta}{T}\right)^{3/2} \frac{1}{\sqrt{N}}. \tag{71.10}$$

The relative fluctuation in energy decreases with a rising number of particles, by the conventional law being proportional to $N^{-1/2}$. However, as the temperature decreases, the fluctuation increases and can become significant. From the physical viewpoint this is explained by the fact that a decrease in temperature is accompanied by a decrease in the effective number of the degrees of freedom ("freezing out" of vibrations, Secs. 48, 53), the result being that in a system with a small number of degrees of freedom fluctuations usually become important.

It should be noted finally that energy fluctuations become rather large in isothermal systems ($C_V \to \infty$). For instance, in a liquid-saturated vapour system boiling occurs at a constant pressure. In this connection the entire boiling process is of a random, fluctuation nature.

Let us calculate fluctuations in a T-P-N system. The X-sum over states has the form (formula (63.35))

$$X(\beta, \gamma) = \int \sum_i dV \exp[-\gamma V - \beta E(i|V)]\, g(i, V).$$

The mean energy and the mean volume are equal to

$$\overline{E} = -\frac{\partial}{\partial \beta} [\ln X(\beta, \gamma)]_\gamma, \quad \overline{V} = -\frac{\partial}{\partial \gamma} [\ln X(\beta, \gamma)]_\beta. \tag{71.11}$$

Energy dispersion and volume dispersion can be calculated in the same way as for the T-V-N system. They are equal to

$$(\mathrm{D}E)^2 = -\left(\frac{\partial \bar{E}}{\partial \beta}\right)_\gamma = T^2\left(\frac{\partial \bar{E}}{\partial T}\right)_\gamma, \tag{71.12}$$

$$(\mathrm{D}V)^2 = -\left(\frac{\partial \bar{V}}{\partial \gamma}\right)_\beta = -T\left(\frac{\partial \bar{V}}{\partial P}\right)_T. \tag{71.13}$$

Let us calculate the derivative $\left(\frac{\partial \bar{E}}{\partial T}\right)_\gamma$. To separate out the heat capacity $\left(\frac{\partial \bar{E}}{\partial T}\right)_V$ we pass in the Jacobian to variables T, V. We have

$$\frac{\partial(\bar{E}, \gamma)}{\partial(T, \gamma)} = \frac{\partial(\bar{E}, \gamma)}{\partial(T, V)}\frac{\partial(T, V)}{\partial(T, \gamma)} = \frac{(\partial \bar{E}/\partial T)_V (\partial\gamma/\partial V)_T - (\partial \bar{E}/\partial V)_T (\partial\gamma/\partial T)_V}{(\partial\gamma/\partial V)_T}$$

$$= C_V - \left(\frac{\partial \bar{E}}{\partial T}\right)_T \frac{\partial(\gamma, V)/\partial(T, V)}{\partial(\gamma, T)/\partial(V, T)}.$$

Let us pass in the second term on the right-hand side to variables T, P, on which the quantity $\gamma = P/T$ depends:

$$\left(\frac{\partial \bar{E}}{\partial T}\right)_\gamma = C_V + \left(\frac{\partial \bar{E}}{\partial V}\right)_T \frac{\partial(\gamma, V)/\partial(P, T)}{\partial(\gamma, T)/\partial(P, T)}$$

$$= C_V + \left(\frac{\partial \bar{E}}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P + \frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_T\right]$$

whence

$$(\mathrm{D}E)^2 = T^2\left\{C_V + \left(\frac{\partial \bar{E}}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P + \frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_T\right]\right\}. \tag{71.14}$$

The derivative $\left(\frac{\partial \bar{E}}{\partial V}\right)_T$ was calculated in Sec. 11:

$$\left(\frac{\partial \bar{E}}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V,$$

and for the energy dispersion in a T-P-N system we obtain

$$(\mathrm{D}E)^2 = T^2\left[C_V + T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V - \frac{P^2}{T}\left(\frac{\partial V}{\partial P}\right)_T - 2P\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{71.15}$$

For an ideal gas, in particular, $\left(\frac{\partial \bar{E}}{\partial V}\right)_T = 0$, hence, energy dispersion is $(\mathrm{D}E)^2 = T^2 C_V$, just as for the T-V-N system. This result is to be expected, since for an ideal gas $\gamma = P/T = R/V$, and the condition $\gamma = \text{const}$ is equivalent to $V = \text{const}$.

Making use of formula (71.13), it is possible to get an expression for fluctuation in density $\rho = m/V$. We have

$$\mathrm{D}\rho = -\frac{m}{V^2}\mathrm{D}V = -\rho\frac{\mathrm{D}V}{V},$$

whence

$$(\mathrm{D}\rho)^2 = -\frac{\rho^2}{V^2} T \left(\frac{\partial V}{\partial P}\right)_T. \tag{71.16}$$

In the case of a T-V-μ system, similar operations lead to the following formulae for the dispersion of energy and number of particles:

$$(\mathrm{D}E)^2 = -\left(\frac{\partial \bar{E}}{\partial \beta}\right)_\alpha, \tag{71.17}$$

$$(\mathrm{D}N)^2 = \left(\frac{\partial \bar{N}}{\partial \alpha}\right)_\beta. \tag{71.18}$$

Let us pass now from the variables $\beta = 1/T$, $\alpha = \mu/T$, to the variables T, μ. We have

$$\left(\frac{\partial \bar{E}}{\partial \beta}\right)_\alpha = \frac{\partial(\bar{E}, \alpha)/\partial(T, \mu)}{\partial(\beta, \alpha)/\partial(T, \mu)} = \frac{(\partial \bar{E}/\partial T)_\mu (\partial \alpha/\partial \mu)_T - (\partial \bar{E}/\partial \mu)_T (\partial \alpha/\partial T)_\mu}{(\partial \beta/\partial T)_\mu (\partial \alpha/\partial \mu)_T}$$

$$= -T^2\left[\left(\frac{\partial \bar{E}}{\partial T}\right)_\mu + \frac{\mu}{T}\left(\frac{\partial \bar{E}}{\partial \mu}\right)_T\right],$$

$$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_\beta = T\left(\frac{\partial \bar{N}}{\partial \mu}\right)_T$$

and, consequently, in a T-V-μ system

$$(\mathrm{D}E)^2 = T^2\left[\left(\frac{\partial \bar{E}}{\partial T}\right)_\mu + \frac{\mu}{T}\left(\frac{\partial \bar{E}}{\partial \mu}\right)_T\right], \tag{71.19}$$

$$(\mathrm{D}N)^2 = T\left(\frac{\partial \bar{N}}{\partial \mu}\right)_T. \tag{71.20}$$

Problems

1. Show that for a harmonic oscillator with frequency ν

$$(\mathrm{D}E_1)^2 = h^2\nu^2 e^{h\nu/T}(e^{h\nu/T} - 1)^{-2} \text{ and } \delta E_1 = e^{h\nu/2T}.$$

Hint. To simplify calculations, take the zero-oscillation energy as reference for energy.

2. Find $(\mathrm{D}E)^2$ and δE for a system of N non-interacting oscillators.

Answer. $(\mathrm{D}E)^2 = N(\mathrm{D}E_1)^2$, $\delta E = N^{-1/2}\delta E_1$.

3. Find $(\mathrm{D}v)^2$ and δv for Maxwell's distribution.

Answer. $(\mathrm{D}v)^2 = \left(3 - \frac{8}{\pi}\right)\frac{T}{m}$, $\delta v = \left(\frac{3\pi}{8} - 1\right)^{1/2}$.

4. Show that the correlation of energy and particle-number fluctuations in a T-V-μ system is equal to $\overline{\Delta E \Delta N} = T\left(\frac{\partial \bar{E}}{\partial \mu}\right)_T$.

Hint. Differentiate the expression for $\bar{E}$ in a T-V-μ system with respect to μ.

72. Fluctuations in Main Thermodynamic Quantities

Let us consider a homogeneous macroscopic system, assuming it as a whole to be closed. It is possible to mentally single out in the system a macroscopic subsystem, small compared to the original system, following two methods: (1) the subsystem contains a fixed number of particles N, but its volume V fluctuates; (2) the subsystem has a fixed volume V, but the number of particles N in it fluctuates. In addition, in contrast to the T-P-N and T-V-μ distributions, an assumption is made that fluctuations in the intensive parameters T, P, μ can take place in the subsystem, and that their values can differ from these in the surrounding medium, T_0, P_0, μ_0.

The probability of the system as a whole (subsystem + surroundings) being in an arbitrary state is, in accordance with Boltzmann's principle, related to the total system entropy S_t by the expression $W \propto e^{S_t}$. Taking account of the fluctuations, this expression can be rewritten to read

$$W = Ae^{\Delta S_t} = Ae^{\Delta S_0 + \Delta S}, \tag{72.1}$$

where ΔS_0 and ΔS are respectively the changes in the entropies of the surroundings and the system, compared to their values in the equilibrium state. Formula (72.1) is sometimes named after Einstein, who was the first to use it to investigate fluctuations.

Let us consider the two cases separately. In the first case, change in the surrounding entropy can be presented in the form

$$\Delta S_0 = \frac{\Delta U_0 + P_0 \Delta V_0}{T_0} = -\frac{\Delta U + P_0 \Delta V}{T_0}. \tag{72.2}$$

Such a representation is feasible due to the fact that we are interested in the fluctuations occurring in the subsystem, while the surrounding medium is assumed to be in equilibrium due to its large size, and gradients of its parameters appear only in the thin surface layer on the interface with the subsystem. Naturally, expressions like (72.2) cannot be used to describe entropy fluctuations in the subsystem, ΔS. The exponent in formula (72.1) is found to be expressed by $\frac{T_0 \Delta S - P_0 \Delta V - \Delta U}{T_0}$.

Assuming the fluctuations to be small, let us expand ΔU into a series in ΔS and ΔV to terms of the second order of smallness:

$$\Delta U = \left(\frac{\partial U}{\partial S}\right)_0 \Delta S + \left(\frac{\partial U}{\partial V}\right)_0 \Delta V + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_0 \Delta S^2 + 2\left(\frac{\partial^2 U}{\partial S\, \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)_0 \Delta V^2\right],$$

where all derivatives of the internal energy are taken in the equilibrium state. Taking into account that $\left(\frac{\partial U}{\partial S}\right)_0 = T_0$ and $\left(\frac{\partial U}{\partial V}\right)_0$

$= -P_0$, we see that all terms linear in ΔS and ΔV in the exponent in formula (72.1) are cancelled out, and this exponent is equal to

$$-\frac{\left(\frac{\partial T}{\partial S}\right)_0 \Delta S^2 + \left(\frac{\partial T}{\partial V}\right)_0 \Delta S\,\Delta V - \left(\frac{\partial P}{\partial S}\right)_0 \Delta V\,\Delta S - \left(\frac{\partial P}{\partial V}\right)_0 \Delta V^2}{2T_0} = \frac{\Delta P\,\Delta V - \Delta T\,\Delta S}{2T_0}.$$

Finally, formula (72.1) reduces to

$$W = A \exp\left[\frac{\Delta P\,\Delta V - \Delta T\,\Delta S}{2T}\right] \tag{72.3}$$

(the subscript 0 for the temperature is omitted below, assuming that T denotes the temperature in the equilibrium state).

In the second case (fixed volume, fluctuating number of particles) the change in the surrounding entropy due to fluctuations in the subsystem is equal to

$$\Delta S_0 = \frac{\Delta U_0 - \mu_0 \Delta N_0}{T_0} = -\frac{\Delta U - \mu_0 \Delta N}{T_0} \tag{72.4}$$

and, in accordance with the above reasoning, we get the formula

$$W = A \exp\left[-\frac{\Delta T\,\Delta S + \Delta\mu\,\Delta N}{2T}\right]. \tag{72.5}$$

There exists one more possibility of separating a subsystem from its surroundings, permitting fluctuations in both the volume and the number of particles—the separation with the aid of a physical boundary layer. Simplest examples of such separation are a droplet of liquid in a vapour, a bubble of gas in a liquid, a crystal in a melt, etc.

We could obtain for such cases a formula for the probability of fluctuations in which, in contrast to (72.3) and (72.5), there would be three terms in the exponent, $\frac{\Delta P \Delta V - \Delta T \Delta S - \Delta\mu \Delta N}{2T}$. In the presence of a physical boundary between the surroundings and the subsystem, however, in addition to volume fluctuations, of paramount importance can be fluctuations in the form of the boundary surface. In this case new thermodynamic degrees of freedom appear (for instance, capillary waves on the boundary surface, changes in the crystal faces), and the problem is complicated considerably. We shall limit ourselves to a consideration of formulae (72.3) and (72.5). The case of a subsystem with a constant number of particles N is discussed in detail in Sec. 112 of [18].

Let us turn to the case when $V = \text{const}$, the number of particles N fluctuates and consider some particular results obtained applying formula (72.5). We select as independent variables T and N; then

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_N \Delta T + \left(\frac{\partial S}{\partial N}\right)_T \Delta N, \quad \Delta\mu = \left(\frac{\partial \mu}{\partial T}\right)_N \Delta T + \left(\frac{\partial \mu}{\partial N}\right)_T \Delta N,$$

and, using the relation $\frac{\partial(T, S)}{\partial(\mu, N)} = -1$, at $V = \text{const}$ (see Sec. 22) we obtain

$$W = A \exp\left[\frac{\frac{\tilde{V}^2}{N}\left(\frac{\partial P}{\partial \tilde{V}}\right)\Delta N^2 - \frac{C_{N,V}}{T}\Delta T^2}{2T}\right], \qquad (72.6)$$

where use was made of the relationships $T\left(\frac{\partial S}{\partial T}\right)_{N,V} = C_{N,V}$ and $\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \tilde{V}\left(\frac{\partial P}{\partial N}\right)_{T,V} = -\frac{\tilde{V}^2}{N}\left(\frac{\partial P}{\partial \tilde{V}}\right)_{T,V}$. It follows from formula (72.6) that the fluctuations in temperature and in the number of particles are independent of each other and obey Gauss' law.

For the root-mean-square deviations and the correlation $\overline{\Delta T\,\Delta N}$ we find (see Mathematical Appendix, AXIV)

$$(\mathsf{D}T)^2 = \frac{T^2}{C_{N,V}}, \quad (\mathsf{D}N)^2 = -\frac{NT}{\tilde{V}^2}\left(\frac{\partial \tilde{V}}{\partial P}\right)_{T,V}, \quad \overline{\Delta T\,\Delta N} = 0. \qquad (72.7)$$

The first two expressions are positive due to the inequalities $C_{N,V} > 0$, $\left(\frac{\partial \tilde{V}}{\partial P}\right)_{T,V} < 0$. The second formula of (72.7) can readily be shown to be equivalent to (71.20). When other selection methods for the independent variables are applied, formula (72.5) is of little help, since at $V = N\tilde{V} = \text{const}$ the volume $\tilde{V}$ depends on the extensive variable N, and, consequently, all intensive parameters T, μ, P, $\tilde{S}$, etc. should be considered as functions of N and of some intensive variable. It is clear that it is more convenient to take temperature as such an intensive variable, and we return to the selection of variables N and T. Let us consider as an example of the Gaussian distribution formula (72.3), selecting as independent variables temperature T and pressure P. Then,

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_P \Delta T + \left(\frac{\partial S}{\partial P}\right)_T \Delta P = \frac{C_P}{T}\Delta T - \left(\frac{\partial V}{\partial T}\right)_P \Delta P,$$

$$\Delta V = \left(\frac{\partial V}{\partial T}\right)_P \Delta T + \left(\frac{\partial V}{\partial P}\right)_T \Delta P.$$

Whence we find for the exponent in formula (72.3) the expression

$$-\frac{(C_P/T)\,\Delta T^2 - 2\,(\partial V/\partial T)_P\,\Delta T\,\Delta P - (\partial V/\partial P)_T\,\Delta P^2}{2T}$$

and, making use of formulae (XIV.10) through (XIV.12), we find

$$(\mathsf{D}T)^2 = \frac{T^2(\partial V/\partial P)_T}{C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2} = \frac{T^2}{C_V},$$

$$(\mathsf{D}P)^2 = \frac{-TC_P}{C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2} = -T\left(\frac{\partial P}{\partial V}\right)_S, \qquad (72.8)$$

$$\overline{\Delta P\,\Delta T} = -\frac{T^2(\partial V/\partial T)_P}{C_P(\partial V/\partial P)_T + T(\partial V/\partial T)_P^2} = \frac{T^2}{C_V}\left(\frac{\partial P}{\partial T}\right)_V.$$

It is useful to pay attention to the fact that, in accordance with formulae (72.7), (72.8), the squares of fluctuations in the intensive quantities $(\mathrm{D}T)^2$ and $(\mathrm{D}P)^2$ are inversely proportional to the number of particles N, and the square of fluctuation in the extensive variable, $(\mathrm{D}N)^2$, is directly proportional to N. Relative fluctuations, however, in both cases are inversely proportional to $\sqrt{N}$. It is clear that all extensive and intensive thermodynamic variables posses similar properties.

Problems

1. Prove the relationships (72.8), using Jacobians.
2. Find (a) $\overline{\Delta T\, \Delta S}$; (b) $(\mathrm{D}S)^2$.

Answer. (a) $\overline{\Delta T\, \Delta S} = T$; (b) $(\mathrm{D}S)^2 = C_p$.

73. Fluctuations in Occupation Numbers in Ideal Gases

This section is devoted to the study of particle-number fluctuations in each quantum state for bosons, fermions and Maxwell (distinguishable) particles. For an ideal gas the distributions of particles for each energy level, ε_i, are independent from each other, and we can write formula (71.20) for each number of particles N_i separately

$$(\mathrm{D}N_i)^2 = T\left(\frac{\partial \overline{N}_i}{\partial \mu}\right)_{T,V}. \tag{73.1}$$

Replacing $\overline{N_i}$ by the expression

$$\overline{N}_i = \frac{g_i}{e^{(\varepsilon_i-\mu)/T}+\zeta},$$

where $\zeta = -1, +1, 0$ for bosons, fermions and distinguishable particles respectively, we obtain

$$(\mathrm{D}N_i)^2 = \frac{g_i e^{(\varepsilon_i-\mu)/T}}{\left(e^{(\varepsilon_i-\mu)/T}+\zeta\right)^2} = \overline{N}_i - \zeta\frac{(\overline{N}_i)^2}{g_i}$$

or

$$(\mathrm{D}N_i)^2 = \overline{N}_i + \frac{(\overline{N}_i)^2}{g_i}, \quad (\mathrm{D}N_i)^2 = \overline{N}_i - \frac{(\overline{N}_i)^2}{g_i}, \quad (\mathrm{D}N_i)^2 = \overline{N}_i, \tag{73.2}$$

for bosons, fermions and distinguishable particles respectively. It follows from the above that relative fluctuations are expressed by

$$\delta N_i = (\overline{N_i})^{-1/2}\left[1+\frac{\overline{N}_i}{g_i}\right]^{1/2}, \quad \delta N_i = (\overline{N}_i)^{-1/2}\left[1-\frac{\overline{N}_i}{g_i}\right]^{1/2},$$

$$\delta N_i = (\overline{N}_i)^{-1/2} \tag{73.3}$$

for bosons, fermions and distinguishable particles respectively.

Knowing the expressions for the chemical potentials of bosons, fermions and distinguishable particles and the corresponding distributions, we can study the behaviour of $\mathsf{D}N_i$ and δN_i, depending on temperature and density $\bar{N}/V$ (see problem to this section). Let us consider a particular case of formula (73.1) for bosons, when the chemical potential is identically equal to zero, and $\varepsilon = h\nu$ (a photon gas, see Sec. 52).

Let us write down formula (73.2) for the frequency band ν, $\nu - d\nu$, replacing g_i by the expression $8\pi\nu^2\, d\nu V/c^3$ and N_i by $dN(\nu)$ to obtain

$$[\mathsf{D}\, dN(\nu)]^2 = dN(\nu)\left[1 + \frac{dN(\nu)\, c^3}{8\pi\nu^2\, d\nu\, V}\right].$$

Multiplying both sides of the above expression by $(h\nu)^2$, we obtain the dispersion of radiant energy in the frequency band ν, $\nu - d\nu$:

$$[\mathsf{D}\, dE(\nu)]^2 = h\nu\, dE(\nu) + \frac{c^3\,[dE(\nu)]^2}{8\pi\nu^2\, d\nu\, V}. \qquad (73.4)$$

Relationship (73.4), first derived by Einstein, has a deep physical meaning. Let us consider the ratio of the second term on the right hand side of Eq. (73.4) to the first term $\mathsf{D}(\nu)$. According to Planck's formula,

$$dE(\nu) = \frac{8\pi h}{c^3}\,\frac{\nu^3\, d\nu\, V}{e^{h\nu/T} - 1},$$

it is equal to

$$\mathsf{D}(\nu) = (e^{h\nu/T} - 1)^{-1} = \frac{dN(\nu)}{dn(\nu)}.$$

It follows that in the limiting case $h\nu/T \gg 1$ the order of magnitude of the ratio is $e^{-h\nu/T}$ and it is small compared with unity, and in the limiting case $h\nu/T \ll 1$ this ratio is proportional to $\frac{T}{h\nu}$ and is large compared with unity. This means that the first term in Eq. (73.4) predominates at high frequencies, when Wien's law is approximately valid (see Sec. 17), and reflects the corpuscular nature of radiation. This is also emphasized by the fact that for bosons and fermions the first term in formulae (73.2) coincides with the classical expression for Maxwell particles in (73.2). On the contrary, the second term in Eq. (73.4) prevails at low frequencies, when the Rayleigh-Jeans law is approximately valid, and it is of a purely wave nature. Einstein obtained the second term, considering radiation in a cavity as a system of electromagnetic standing waves. This reasoning is, however, rather cumbersome and not outlined here [24].

Thus, it was shown that in the region of high frequencies $h\nu/T \gg 1$ and low light intensities $\mathsf{D}(\nu) \ll 1$ radiation behaves as an ideal gas of non-interacting particles—light quanta. On the contrary, in the region of low frequencies $h\nu/T \ll 1$ and high intensities

$\mathbf{D}(\nu) \gg 1$ radiation behaves as a system of classical electromagnetic waves. Thus, the wave-particle duality of light manifests itself markedly in phenomena associated with light fluctuations.

Let us consider the fluctuations of radiation in Wien's region from a somewhat different viewpoint and find the probability of fluctuation in a given volume of radiant energy, using Einstein's formula for the probability of fluctuation

$$\frac{W}{W_0} = e^{[S(V)-S(V_0)]/T}, \tag{73.5}$$

where $S(V_0)$ = entropy in the equilibrium state — radiation occupies an equilibrium volume V_0;

$S(V)$ = entropy in the state of fluctuation—radiation occupied volume V.

According to formula (35.5) for entropy in the frequency band $(\nu, \nu + d\nu)$, we have

$$dS(\nu) = V\,dn(\nu)\{[\mathbf{D}(\nu)+1]\ln[\mathbf{D}(\nu)+1] - \mathbf{D}(\nu)\ln\mathbf{D}(\nu)\}.$$

In Wien's region $\mathbf{D}(\nu) \ll 1$, and the above expression reduces to

$$dS(\nu) = V\,dn(\nu)\,\mathbf{D}(\nu)[1 - \ln \mathbf{D}(\nu)].$$

The radiant energy in the same spectral range is

$$dE(\nu) = V\,dn(\nu)\,\mathbf{D}(\nu)\,h\nu.$$

Eliminating $\mathbf{D}(\nu)$ from these formulae, we obtain

$$dS(\nu) = \frac{dE(\nu)}{h\nu}\left[1 - \ln\left(\frac{dE(\nu)}{V h\nu\, dn(\nu)}\right)\right].$$

The entropy difference $dS(V_0) - dS(V)$ is expressed by

$$dS(V_0) - dS(V) = \frac{dE(\nu)}{h\nu}\ln\left(\frac{V_0}{V}\right).$$

Hence, according to (73.5), the probability of fluctuation is equal to

$$\frac{W}{W_0} = \left(\frac{V}{V_0}\right)^{dE(\nu)/h\nu} = \left(\frac{V}{V_0}\right)^{dN(\nu)}.$$

This relationship is rather simply interpreted: if volume V_0 contains $dN(\nu)$ photons, the probability of finding each photon in a smaller volume V is equal to V/V_0 and for all photons it equals $(V/V_0)^{dN(\nu)}$ owing to their independence. This emphasizes once more that prevailing in Wien's region are the corpuscular properties of light.

74. Fluctuation Limit of Sensitivity of Measuring Instruments. Nyquist's Theorem

Fluctuations taking place in measuring instruments can limit the measurement accuracy of sufficiently sensitive instruments. It is clear that a limit of measurement accuracy is reached when the fluctua-

tion (Brownian) displacements of the moving parts of a measuring instrument become of the same order of magnitude as the displacement caused by the effect being measured.

Let us consider by way of a simple example a torsion balance, comprising a tiny mirror usually suspended from a quartz thread. Let the torsional modulus of the thread be equal to $a = \frac{\pi^2 d^4 G}{8l}$, where G is the shear modulus. Then, the moment of force acting upon the thread is related to the torsion angle φ by the formula $M = a\varphi$, and the potential energy of the twisted thread $\mathcal{U} = a\varphi^2/2$. According to Boltzmann's formula, the mean square of the fluctuation angle $\overline{\varphi^2}$ is equal to

$$\overline{\varphi^2} = \frac{\int_{-\infty}^{\infty} \varphi^2 e^{-a\varphi^2/2T}\, d\varphi}{\int_{-\infty}^{\infty} e^{-a\varphi^2/2T}\, d\varphi} = \frac{T}{a}. \tag{74.1}$$

The quantity $\sqrt{\overline{\varphi^2}} = (T/a)^{1/2}$, obviously, represents the *limit of sensitivity*. This result can also be obtained directly from the classical equipartition law, according to which the potential energy of an oscillator $a\varphi^2/2$ is accounted for on the average by the energy $T/2$. At room temparature and $a \sim 10^{-5}$ erg, $\sqrt{\overline{\varphi^2}} \sim 10^{-4}$ rad, which predetermines for many instruments the real limit of sensitivity for a single measurement. Repeated measurements permit, of course, to reduce many times this limit, eliminating the isotropic fluctuation background.

As a second example let us consider a fluctuation emf $\mathcal{E}(T)$ in an unbranched circuit with an inductance L and an ohmic resistance R. This electromotive force is due to the fluctuation movements of electrons in the conductor, it will be assumed below that the average value of emf is equal to zero, $\overline{\mathcal{E}(T)} = 0$. It will also be assumed that the condition that the current is quasi-stationary is satisfied, i.e. that the frequency ω is small compared with c/l, where l is the length of the circuit. Hence, firstly, current intensity is the same in all sections and, secondly, it is in order to apply Kirchhoff's law $IR = -L\dot{I} + \mathcal{E}(T)$, rewritten to read

$$\dot{I} + \gamma I = L^{-1}\mathcal{E}(T), \tag{74.2}$$

where $\gamma = R/L$. It should be noted that Eq. (74.2) allows a mechanical interpretation. Indeed, replacing $I \to v$, $L \to m$, $R \to \beta$, $\mathcal{E}(T) \to f(t)$, we obtain the equation

$$m\dot{v} + \beta v = f(t),$$

expressing Newton's second law for a Brownian particle in a random force field $f(t)$ and referred to as *Langevin's equation*. Integrating Eq. (74.2), we obtain

$$I(t) = I(0)\, e^{-\gamma t} + \frac{1}{L} \int_0^t \mathcal{E}(u)\, e^{\gamma(u-t)}\, du.$$

Let us introduce the *correlation function* of the random electromotive force, $\varphi(\tau)$, determining it as the mean value of

$$\varphi(\tau) = \overline{\mathcal{E}(t)\, \mathcal{E}(t+\tau)}, \tag{74.3}$$

where the averaging is performed over t. It depends only on τ by virtue of homogeneity of time.

Let us calculate the average value of squared current intensity:

$$\overline{I^2(t)} = I^2(0)\, e^{-2\gamma t} + \frac{1}{L^2} \int_0^t \int_0^t \overline{\mathcal{E}(u)\, \mathcal{E}(v)}\, e^{\gamma(u+v-2t)}\, du\, dv.$$

Passing in the above expression to the variables $\tau = u - v$, $\tau' = u + v$ (the Jacobian $|\partial(u, v)/\partial(\tau, \tau')| = 1/2$), we obtain

$$\overline{I^2(t)} = I^2(0)\, e^{-2\gamma t} + \frac{e^{-2\gamma t}}{2L^2} \int_0^{2t} e^{\gamma\tau'}\, d\tau' \int_{-t}^{t} \varphi(\tau)\, d\tau$$

$$= I^2(0)\, e^{-2\gamma t} + \frac{1 - e^{-2\gamma t}}{2RL} \int_{-t}^{t} \varphi(\tau)\, d\tau. \tag{74.4}$$

At $t \gg \gamma^{-1} = L/R$ we have

$$\overline{I^2(t)} = \frac{1}{2RL} \int_{-t}^{t} \varphi(\tau)\, d\tau \tag{74.5}$$

In the limit of large t the system tends to thermodynamic equilibrium and in this state the energy per one magnetic degree of freedom must be equal to $T/2$. Consequently, we have

$$\frac{L\overline{I^2}}{2} = \frac{1}{4R} \int_{-t}^{t} \varphi(\tau)\, d\tau = \frac{T}{2},$$

whence

$$\int_{-t}^{t} \varphi(\tau)\, d\tau = 2RT. \tag{74.6}$$

Since relationship (74.6) is valid at sufficiently large t and the function $\varphi(\tau)$ is symmetric due to time homogeneity, the solution of

Eq. (74.6) is

$$\varphi(\tau) = 2RT\delta(\tau) \tag{74.7}$$

(in principle, the right-hand side must contain a delta-function "spread" over the interval $\Delta\tau \propto \gamma^{-1}$).

Let us relate now the correlation function $\varphi(\tau)$ and the spectral characteristic of a random electromotive force. We expand $\mathcal{E}(t)$ into a Fourier integral

$$\mathcal{E}(t) = \int_{-\infty}^{\infty} A(\omega)\, e^{i\omega t}\, d\omega, \tag{74.8}$$

where, by virtue of the fact that $\mathcal{E}(t)$ is real-valued, the Fourier coefficients $A(\omega)$ must satisfy the condition

$$A(-\omega) = A^*(\omega). \tag{74.9}$$

Substituting expansion (74.8) into (74.3), we get

$$\varphi(\tau) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} A(\omega')\, A(\omega) \exp[i(\omega+\omega')t + i\omega\tau]\, d\omega\, d\omega'. \tag{74.10}$$

Since expression (74.10) must not depend on t, the integrand must differ from zero only at $\omega' = -\omega$ and, consequently,

$$\overline{A(\omega')\, A(\omega)} = \mathcal{E}^2(\omega)\, \delta(\omega+\omega'); \tag{74.11}$$

relation (74.11) defines simultaneously the quantity $\mathcal{E}^2(\omega)$. It follows from the above that

$$\varphi(\tau) = \int_{-\infty}^{\infty} \mathcal{E}^2(\omega)\, e^{i\omega\tau}\, d\omega. \tag{74.12}$$

This formula, relating the correlation function $\varphi(\tau)$ and the spectral composition of a random electromotive force, is referred to as *Wiener-Khintchine formula* (for greater detail see [25]). In particular, at $\tau = 0$ we have

$$\varphi(0) = \overline{\mathcal{E}^2(t)} = \int_{-\infty}^{\infty} \mathcal{E}^2(\omega)\, d\omega. \tag{74.13}$$

Comparing formulae (74.12) and (74.7) and using the delta-function representation, $\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\alpha x}\, dx = \delta(\alpha)$, we obtain the expression for $\mathcal{E}^2(\omega)$:

$$\mathcal{E}^2(\omega) = \frac{RT}{\pi}. \tag{74.14}$$

referred to as the *Nyquist theorem*. Since $\mathcal{E}^2(\omega)$ is independent of ω, the fluctuation electromotive force is nothing but a white noise, the same at all frequencies, with the intensity of $\mathcal{E}^2(\omega)$ being proportional to temperature and resistance. All these properties are well corroborated by experiment. A further generalization of the Nyquist theorem is the so-called *fluctuation-dissipation theorem* (Callen-Walton theorem) relating energy fluctuations and dissipation in a thermodynamic system (see [18], [25]).

Problems

1. A homogeneous cylindrical rod, having a base diameter d, height h and mass m, stands on an ideally levelled platform. At what temperature will the probability of the rod falling down due to fluctuations of the position of the centre of gravity become comparable with unity? Calculate this temperature at $d = 10^{-1}$ cm, $h = 100$ cm, $m = 2$ g.

Answer. $T \sim \frac{mgd^2}{2h} \sim 10^{15}$ K.

2. Find the mean squared charge of a capacitor with capacitance C short-circuited through resistance R without electromotive force.

Answer. $\overline{q^2} = T/C$.

3. Prove the Nyquist theorem for an unbranched circuit consisting of a capacitor with capacitance C and resistance R.
4. In a homogeneous gas with a particle density n find (a) the probability $W(r)$ that the nearest neighbour is arranged at a distance r from a chosen particle; (b) the mean particle spacing $\bar{r}$ and its absolute $(Dr)^2$ and relative δr fluctuations.

Hint. For the function $W(r)$ the following equation is true:

$$W(r) = \left(1 - \int_0^r W(r')\,dr'\right) 4\pi r^2 n.$$

Answer. (a) $W(r) = 4\pi n r^2 \exp\left[-4\pi n r^3/3\right]$;

(b) $\bar{r} = \left(\frac{3}{4\pi}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) n^{-1/3}$,

$$(Dr)^2 = \left(\frac{3}{4\pi}\right)^{2/3} \left[\Gamma\left(\frac{5}{3}\right) - \Gamma^2\left(\frac{4}{3}\right)\right] n^{-2/3},$$

$$\delta r = \frac{\left[\Gamma\left(\frac{5}{3}\right) - \Gamma^2\left(\frac{4}{3}\right)\right]^{1/2}}{\Gamma\left(\frac{4}{3}\right)}.$$

CHAPTER VIII

PHASE TRANSITIONS

In Secs. 26 through 28, Chap. II, phase transitions were discussed from the viewpoint of phenomenological thermodynamics. This chapter is devoted to the study of phase transitions within the framework of a statistical description. First, we shall examine a rather attractive theory developed by Lee and Yang. Although this theory almost fails to offer new possibilities of solving concrete problems, it leads, as will be shown below, to a clear understanding of how the possibility of phase transitions originates from the mathematical formalism of the theory.

75. The Lee-Yang Theory

The thermodynamic functions of a system must have at the phase transition point some peculiar features: the functions or their derivatives must have at that point finite or infinite discontinuity jumps. In statistical physics all thermodynamic functions are expressed in terms of corresponding partition functions or integrals of states.

Let us consider a non-ideal gas confined within volume V, assuming that the repulsive forces between closely spaced gas molecules increase so rapidly that the number of molecules n in the volume V cannot exceed some large but finite number N.

Let us write down the expression for the Q-sum of a grand canonical ensemble (T-V-μ ensemble) in the form (65.4):

$$Q = \sum_{n=0}^{N} z^n Q_n, \tag{75.1}$$

where $z = e^{\beta\mu}$ is activity, and

$$Q_n = \frac{1}{\lambda^{3n} n!} Z_n = \frac{1}{\lambda^{3n} n!} \int d^3 r_1 \ldots d^3 r_n \exp\left[-\beta \sum_{i,k} u(r_{ik}) \right]$$

[see formula (65.4)]. All thermodynamic quantities can be expressed in terms of the Q-sum. We have

$$\Omega = -T \ln Q, \tag{75.2}$$

$$P = \frac{T}{V} \ln Q. \tag{75.3}$$

Let us also find the expression for $1/\omega = N/V$. The number of particles is expressed in terms of Q by the formula $N = -\frac{\partial \Omega}{\partial \mu} = \frac{T \partial (\ln Q)}{\partial \mu}$. Differentiating with respect to z, we obtain $N = \frac{z \partial (\ln Q)}{\partial z}$, whence

$$\frac{1}{\omega} = \frac{z}{V} \frac{\partial}{\partial z} (\ln Q). \tag{75.4}$$

Eliminating from formulae (75.3) and (75.4) parameter z, we can in principle find the equation of state $f(P, \omega, T) = 0$.

From formulae (75.3), (75.4) it follows that thermodynamic quantities can have some singularities only at the points where Q either has singularities or vanishes (singular point for $\ln Q$). It can be seen from formula (75.1), however, that Q is a polynomial of degree N in z with positive coefficients Q_n and, consequently, has no singularities at any finite real or complex values of z. It is for the same reason that the Q-sum has no zeros on the positive real semiaxis, and its complex zeros are complex conjugates (Fig. 97). For this reason, according to Lee and Yang, the only possible explanation why phase transitions are possible in some physical systems consists in the assumption that in passing to the thermodynamic limit $N \to \infty$, $V \to \infty$, $\omega = V/N$ is finite, when the number of zeros in the Q-sum increases infinitely, the zeros of the Q sum can appear at some points on the real z-axis. The corresponding points will be the phase-transition points.

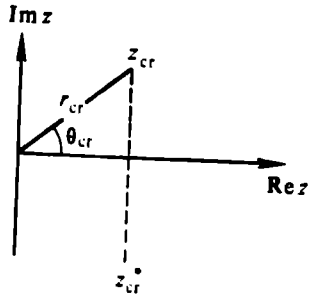


FIG. 97

Let z_k and z_k^* be the complex conjugate roots of the Q-sum. Since the free term of polynominal $Q(z)$ is equal to unity, then

$$Q(z) = \prod_k \left(1 - \frac{z}{z_k}\right)\left(1 - \frac{z}{z_k^*}\right)$$

We denote by r_k and θ_k the modulus and the argument of a complex number z_k, $z_k = r_k e^{i\theta_k}$, $z_k^* = r_k e^{-i\theta_k}$. Expression for Q becomes

$$Q = \prod_k \frac{z^2 + z_k^2 - 2r_k z \cos\theta_k}{r_k^2} = \prod_k \frac{|z - z_k|^2}{r_k^2} \quad (z > 0),$$

and for the Ω-potential, pressure and reciprocal volume formulae (75.2) through (75.4) are used to obtain

$$\Omega = -2T \sum_k [\ln|z - z_k| - \ln r_k],$$

$$P = \frac{2T}{V} \sum_k [\ln|z - z_k| - \ln r_k], \quad \frac{1}{\omega} = \frac{2z}{V} \frac{\partial}{\partial z} \left(\sum_k \ln|z - z_k|\right).$$

These formulae permit a simple electrostatic analogy. Suppose that infinitely long uniformly charged threads (with a linear charge density 1) pass through points z_k of a complex plane z perpendicular to

this plane. Then, as is known from electrostatics, the expression

$$\varphi = 2\tau \ln | z - z_k | = 2\tau \ln (z^2 + r_k^2 - 2r_k z \cos \theta_k)^{1/2}$$

represents the potential of a field created by such a thread at the point z on the real positive semiaxis. Thus, the Ω-potential and pressure can be interpreted as the electrostatic potential $\varphi(z)$, created by the totality of charged threads arranged at points z_k on the upper half-plane z with linear charge densities equal to $-T$ and T/V respectively. The expression $\frac{1}{\omega(z)}$ can be interpreted as the z-component of electrostatic field intensity.

Let us assume that at the thermodynamic limit the zeros of the Q-sum fill a certain line intersecting the positive real semiaxis z (Fig. 98). We denote by $\frac{dn}{ds}$ the number of zeros per unit length of this line (ds is the element of the arc length of this line, measured from some arbitrary point). From the viewpoint of the electrostatic analogy, this means that the threads form at the limit a charged surface with a surface charge density $\sigma(s) = n(s)\,\tau$. As is known from electrostatics, when passing through this surface the field potential varies continuously, while the normal component of intensity undergoes a discontinuity jump equal to $4\pi\sigma$.

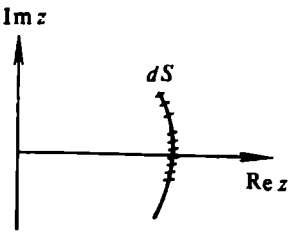


FIG. 98

We arrive in this case to a first-order phase transition: the Ω-potential and the pressure vary continuously, and the molar volume ω undergoes a discontinuity jump.

Let us prove three important inequalities.

1. The inequality $P > 0$ follows from the fact that with real z all factors in formula (75.2) are positive [$Q(z) > 1$].

2. The inequality $\frac{\partial P}{\partial z} > 0$ stems from the fact that $\frac{\partial P}{\partial z}$ differs from $\frac{1}{\omega(z)}$ only in a positive factor.

3. $\frac{\partial \omega}{\partial z} \leqslant 0$. In fact,

$$\frac{\partial \omega}{\partial z} = \frac{\partial}{\partial z}\left(\frac{V}{\bar{n}}\right) = -\frac{V}{(\bar{n})^2}\frac{d\bar{n}}{dz} = -\frac{TV}{(\bar{n})^2 z}\frac{\partial \bar{n}}{\partial \mu}$$

and, using the formula $\overline{\Delta n^2} = \frac{T\partial \bar{n}}{\partial \mu}$, we obtain

$$\frac{\partial \omega}{\partial z} = -\frac{V\overline{\Delta n^2}}{z(\bar{n})^2} \leqslant 0.$$

Further reasonings are based on the two theorems proved by Lee and Yang. The first of the theorems states that at the thermodynamic limit, at any positive z, the expression $\frac{\ln Q}{V}$ tends to a finite limit independent of the form of volume V, and this limit is a continuous non-decreasing function of z.

According to the second Lee-Yang theorem, for all z pertaining to the domain containing a segment of the positive real semiaxis and the Q-sum free of zeros, $P(z) = \frac{T \ln Q}{V}$ tends to a limit at $V \to \infty$ uniformly with respect to z, and the limit function $P^{(\infty)}(z)$ is an analytical function of z. The proof of the two theorems is rather simple, but somewhat involved, and we refer the reader to other sources (for instance, [10]).

Let us first consider the region of the complex plane z associated with the second Lee-Yang theorem. Because of the uniform convergence to the limit of the function $V^{-1} \ln Q$, the operations of passing to the limit $V \to \infty$ and differentiating with respect to z in formula (75.4) can be rearranged, and Eqs. (75.2) and (75.3) remain true after

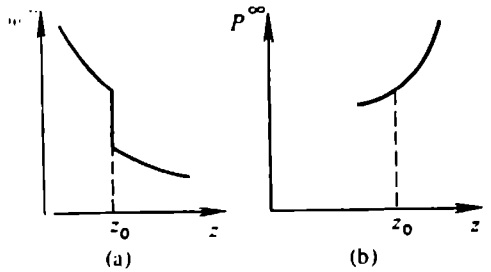


FIG. 99

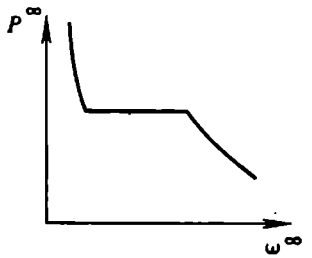


FIG. 100

passing to the limit. In particular, the inequalities 1, 2, 3 also remain valid. Consequently, at points of the positive real semiaxis z belonging to the region under consideration, pressure is a continuous monotonically increasing function of z, which agrees with the behaviour of one phase of a substance.

Let now the line of zeros of $Q(z)$ with a density of zeros $\frac{dn}{ds} \neq 0$ cross the real axis at some point z_0 at the thermodynamic limit. Then, as was shown above, the function $P^{(\infty)}(z)$ varies continuously at that point, while its derivative with respect to z and $\omega^{(\infty)}(z)$ have finite discontinuity jumps, with the quantity $\omega^{(\infty)}(z)$ [Fig. 99(*a*)] diminishing as point z_0 is passed from the left to the right, and the derivative $dP^{(\infty)}/dz$ increasing [Fig. 99(*b*)], as follows from inequality 3. Elimination of the parameter z leads to a dependence $P^{(\infty)}$

on $\omega^{(\infty)}$ shown in Fig. 100, typical of a first-order phase transition.

A case is, however, possible when the density of zeros $\frac{dn}{ds}$ tends to zero as the point z_0 on the real axis is approached. At the thermodynamic limit, an isolated zero of the Q-sum gets on the real semiaxis.

From the viewpoint of the electrostatic analogy this means that the density of charges and the discontinuity jumps of the derivative of pressure $dP^{(\infty)}/dz$ and volume $\omega^{(\infty)}$ with it vanish. If in this case, however, the derivatives $\frac{\partial^2 P^{(\infty)}}{\partial z^2}$ and $\frac{d\omega^{(\infty)}}{dz}$ undergo discontinuity jumps, we are dealing with a second-order phase transition.

It should be noted in concluding this section that the Lee-Yang theory does not give any recipe of solution for problems in phase transitions, since it is easier to find a complete solution of a statistical problem than to discover the arrangement of Q-sum zeros even at the thermodynamic limit.

Problem

Consider a non-physical example, when $Q(z)$ is given by the formula $Q = (1+z)^{N\omega/2}(1-z^{N\omega/2})(1-z)^{-1}$; ω is dimensionless. (a) Show that at the thermodynamic limit the Q-sum has a root $z = 1$. (b) Find the Ω-potential and the equation of state. (c) Describe the distribution of charges in the electrostatic analogy.

Answer. (a) The zeros of the Q-sum lie at points $z_0 = -1$ (zero of multiplicity $N\omega/2$) and $z_k = e^{i4\pi k/N}$, $k = 1, 2, \ldots, N\omega/2 - 1$.

$$\text{(b)}\quad \Omega^{(\infty)} = -\frac{NT\omega}{2}\begin{cases}\ln(1+z), & z<1,\\ \ln[(1+z)z], & z>1,\end{cases}$$

$$\omega^{(\infty)}(z) = \begin{cases}\dfrac{2(z+1)}{z}, & z<1,\\ \dfrac{2(z+1)}{2z+1}, & z>1,\end{cases}$$

$$P^{(\infty)}(\omega^{(\infty)}) = \frac{T}{2}\begin{cases}\ln\dfrac{\omega^{(\infty)}}{\omega^{(\infty)}-2}, & \omega^{(\infty)}>4,\\ \ln 2, & 4>\omega^{(\infty)}>\dfrac{4}{3},\\ \ln\dfrac{\omega^{(\infty)}(2-\omega^{(\infty)})}{4(\omega^{(\infty)}-1)^2}, & \dfrac{4}{3}>\omega^{(\infty)}>1.\end{cases}$$

76. Critical Exponents and Phenomenological Inequalities for Them

This section prepares the reader for the consideration in the following sections of concrete problems in the theory of phase transitions. We shall introduce the definitions of some essential parameters characterizing the behaviour of a system near the phase-transition points.

The first physical system to be examined in Sec. 77 within the framework of van der Waals' approximation is the liquid-gas system in the vicinity of its critical point T_{cr}. At temperatures below the critical the important characteristic of this system is the difference in the molar volumes of the gas and the liquid, $V_2 - V_1$, or the difference (in the vicinity of T_{cr}) in the densities of the liquid and gas, $\rho_1 - \rho_2$, proportional to it. As the critical point is approached, this difference diminishes and tends to zero as $T \to T_{cr}$. To characterize the rate of this decrease, let us introduce the critical exponent β:

$$\rho_1 - \rho_2 = A\tau^{\beta}[1 + O(\tau)], \tag{76.1}$$

where $\tau = (T_{cr} - T)/T_{cr}$, A is a constant and the symbol $O(\tau)$ denotes an infinitesimal (at least of the order of τ).

The other characteristic physical quantity with a singularity at the critical point is the isothermal compressibility, $K_T = V^{-1}\left|\left(\frac{\partial V}{\partial P}\right)_T\right|$, which becomes infinite at the critical point. The rate of increase in K_T near the critical point will be characterized by two critical exponents γ and γ':

$$K_T = \begin{cases} B'\tau^{-\gamma'}[1 + O(\tau)], & T < T_{cr}, \\ B(-\tau)^{-\gamma}[1 + O(\tau)], & T > T_{cr}. \end{cases} \tag{76.2}$$

One more pair of critical exponents α and α' is introduced to characterize the behaviour of the heat capacity C_V as the critical point is approached along the critical isochore. These exponents are introduced by means of the formulae

$$C_V = \begin{cases} D'\tau^{-\alpha'}[1 + O(\tau)], & T < T_{cr}, \\ D(-\tau)^{-\alpha}[1 + O(\tau)], & T > T_{cr}. \end{cases} \tag{76.3}$$

It must, however, be stipulated that the case $\alpha = 0$ ($\alpha' = 0$) can stand for two completely different physical situations: the heat capacity C_V can have a discontinuity jump at the critical point [C_V], and can become infinite, following a logarithmic law $C_V \propto \ln|\tau|$.

Let us introduce, finally, one more critical exponent, characterizing the rate at which pressure P approaches the critical value P_{cr}, depending on the difference $\rho - \rho_{cr}$ on the critical isotherm. This

exponent is specified by the formula

$$P - P_{cr} = F \mid \rho - \rho_{cr} \mid^{\delta} \operatorname{sign} (\rho - \rho_{cr}) \times \left[1 + O\left(\frac{\rho - \rho_{cr}}{\rho_{cr}}\right)\right], \quad T = T_{cr}. \quad (76.4)$$

The factor sign $(\rho - \rho_{cr})$ must be introduced since the derivative $\left(\frac{\partial P}{\partial \rho}\right)_T$ is always non-negative.

In addition to the exponents α, α', β, γ, γ', δ, several more similar quantities are introduced, characterizing the behaviour in the vicinity of phase transition of the derivatives of Gibbs' potential with respect to pressure, the correlation functions, etc. We shall limit ourselves, however, to the consideration of the critical exponents introduced in this section.

The second physical system to be examined in Secs. 78, 79 is a magnetizing substance, which is a ferromagnetic at temperatures below some temperature that is characteristic of the given substance, the Curie point T_c. In the absence of an applied field, the ferromagnetic possesses spontaneous magnetization M, at $T > T_{cr}$ it loses its ferromagnetic properties and behaves as a paramagnetic ($M = 0$ at $H = 0$). Notwithstanding the fact that the physical processes occurring in a liquid-gas system have nothing in common with the processes occurring in a magnetic, there exists a far reaching formal similarity between the behaviour of the parameters characterizing these two systems. In particular, spontaneous magnetization is rather similar to the difference $\rho_1 - \rho_2$ in that the two quantities tend to zero as $T \to T_{cr} - 0$ and do not exist at temperatures above the phase-transition point. In this connection it is customary to characterize the rate of decrease in M as the critical temperature is approached by the critical exponent denoted by the same symbol β as in formula (76.1):

$$M = A_m \tau^{\beta} [1 + O(\tau)]. \quad (76.5)$$

The quantity which is similar to compressibility increases to infinity as the Curie point is approached is the susceptibility $\chi_m = \left(\frac{\partial M}{\partial H}\right)_T$. The rate of increase in susceptibility as $T \to T_{cr}$ is characterized by the exponents denoted, as in formula (76.2), by γ and γ':

$$\chi_m = \begin{cases} B'_m \tau^{-\gamma'} [1 + O(\tau)], & T < T_{cr}, \\ B_m (-\tau)^{\gamma} [1 + O(\tau)], & T > T_{cr}. \end{cases} \quad (76.6)$$

The behaviour of the heat capacity C_H (which is more convenient to use than C_M) is characterized, just as for the liquid-gas system

In formula (76.3), by the critical exponents α and α':

$$C_H = \begin{cases} D'_m \tau^{-\alpha'} [1 + O(\tau)], & T < T_{cr}, \\ D_m (-\tau)^{-\alpha} [1 + O(\tau)], & T > T_{cr}. \end{cases} \quad (76.7)$$

Finally, the dependence of $P - P_{cr}$ on $\rho - \rho_{cr}$ in a gas-liquid system is replaced for a magnetic system by the dependence of H on M along the critical isotherm and is characterized by an exponent denoted, as in formula (76.4), by δ:

$$H = F_m M^{\delta} [1 + O(M)]. \quad (76.8)$$

Phenomenological thermodynamics provides the proof of a number of inequalities relating the critical exponents. The proof of only one such inequality, $\alpha' + 2\beta + \gamma' \geqslant 2$, will be given below, considering a magnetic system by way of example, and proceeding from the relationship between the heat capacities C_H and C_M,

$$C_H - C_M = T \left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H^2 \quad (76.9)$$

(see Sec. 15). Since $C_M \geqslant 0$, just as $C_V \geqslant 0$, this is the condition for thermodynamic stability (see Sec. 25), then it follows from (76.9) that

$$C_H \geqslant T \left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H^2 = \frac{T \left(\frac{\partial M}{\partial T}\right)_H^2}{\chi_m}. \quad (76.10)$$

Near the Curie point, but below it, making use of the expansions in formulae (76.5) through (76.7), we obtain from (76.10) $\tau^{-\alpha'} \geqslant \Pi \tau^{2\beta+\gamma'-2}$, where Π is composed of all factors that are independent of τ in formula (76.10). Since the last inequality must hold for an infinitesimal τ, we have that $-\alpha' \leqslant 2\beta + \gamma' - 2$, or

$$\alpha' + 2\beta + \gamma' \geqslant 2. \quad (76.11)$$

Inequality (76.11) is called the *Rushbrooke-Coopersmith inequality* and it can also be proved in a similar manner for a liquid-gas system. It is also possible to prove in a rather involved way the *Griffith inequality* [26]

$$\alpha' + \beta(1 + \delta) \geqslant 2, \quad (76.12)$$

both for liquid-gas and magnetic systems.

77. Critical Point for the van der Waals Gas

We shall return in this section to the van der Waals equation and concentrate on the vicinity of the critical point.

In doing so, in accordance with the requirements for thermodynamic stability, at pressures below the critical, we shall correct the equation of state and replace the van der Waals isotherms with the

humps and valleys by the real isobar-isotherms, plotted according to the condition for the equality of chemical potentials $\mu_1 = \mu_2$ or Maxwell's equal area rule equivalent to it. This means that inside the dome-shaped curve ACB (Fig. 101) the system will be considered as a two-phase one, consisting of an x fraction of vapour and a $1 - x$ fraction of liquid, where x is determined by the lever rule (see Sec. 12). In this case the van der Waals "vapour" and the van der Waals "liquid" obey the van der Waals equation with the additional condition that the points representing the states of pure "vapour" lie on the curve CB, and the points representing the states of pure "liquid" lie on the curve AC.

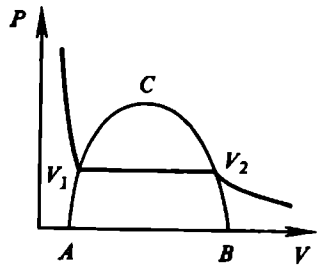


FIG. 101

Our goal is to study the behaviour of thermodynamic quantities in the region close to the critical point C and, in particular, to find the critical exponents. Let us proceed from the van der Waals equation in the dimensionless form

$$\left(\tilde{P}+\frac{3}{\tilde{V}^2}\right)(3\tilde{V}-1)=8\tilde{T}, \tag{77.1}$$

where $\tilde{P} = P/P_{cr}$, $\tilde{V} = V/V_{cr}$ and $\tilde{T} = T/T_{cr}$, and the critical parameters are $V_{cr} = 3b$, $P_{cr} = \frac{a}{27b^2}$, $T_{cr} = \frac{8a}{27N_A b}$ (see Sec. 17).

To investigate the vicinity of the critical point, we assume

$$\tilde{P} = 1 + \pi, \quad \tilde{V} = 1 + \omega, \quad \tilde{T} = 1 - \tau, \tag{77.2}$$

where π, ω and τ are small compared with unity. Upon simple computations, retaining the lowest powers of infinitesimals, we obtain the equation

$$\pi = -4\tau + 6\tau\omega - \frac{3}{2}\omega^3, \tag{77.3}$$

describing the van der Waals isotherms in close vicinity of the critical point. In particular, at $\tau = 0$ we obtain the equation of the critical isotherm in the form of a cubic parabola $\pi = -\frac{3}{2}\omega^3$, and consequently, the exponent for the van der Waals gas $\delta = 3$.

Let us calculate the compressibility of a gas near T_{cr}. We have

$$K_T = \frac{1}{V}\left|\left(\frac{\partial V}{\partial P}\right)_T\right| = \frac{1}{P_{cr}(1+\omega)}\left|\left(\frac{\partial \omega}{\partial \pi}\right)_\tau\right| = \left[P_{cr}(1+\omega)\left(\frac{\partial \pi}{\partial \omega}\right)_\tau\right]$$

and, using formula (77.3), we find approximately

$$K_T = \left[P_{cr} \left(6\tau - \frac{9}{2} \omega^2 \right) \right]^{-1}.$$

In particular, on the critical isochore $\omega = 0$, $K_T \propto \tau^{-1}$, whence we obtain $\gamma' = 1$. To find the difference $\frac{\rho_1 - \rho_2}{\rho_{cr}} \approx \frac{V - V_1}{V_{cr}} = \omega_2 - \omega_1$, in addition to Eq. (77.3) which holds both for ω_1 and ω_2,

$$\pi = -4\tau + 6\tau\omega_2 - \frac{3}{2}\omega_2^3, \quad \pi = -4\tau + 6\tau\omega_1 - \frac{3}{2}\omega_1^3, \qquad (77.4)$$

we must use Maxwell's equal area rule in the form

$$\int_{V_1}^{V_2} P' \, dV = P (V_2 - V_1) \qquad (77.5)$$

[P' denotes the varying pressure on the van der Waals isotherm, and P the same initial and final pressures on the isotherm-isobar V_1V_2 (Fig. 101)].

Passing over to dimensionless variables π, ω, we obtain from formula (77.5)

$$\int_{\omega_1}^{\omega_2} \pi' \, d\omega = \pi (\omega_2 - \omega_1)$$

and, using Eq. (77.3), we find

$$-4\tau + 3\tau (\omega_2 + \omega_1) - \frac{3}{8} (\omega_2 + \omega_1) (\omega_2^2 + \omega_1^2) = \pi. \qquad (77.6)$$

Substituting expressions (77.4) into the right-hand side of (77.6) and summing up the expressions obtained, we obtain

$$(\omega_2 + \omega_1) (\omega_2 - \omega_1)^2 = 0,$$

from which it follows that

$$\omega_2 = -\omega_1. \qquad (77.7)$$

Subtracting from the first equation of (77.4) the second and taking into account (77.7), we obtain

$$\omega_2 = -\omega_1 = 2\sqrt{\tau}, \qquad (77.8)$$

from which it follows that in the van der Waals theory the exponent β is equal to 1/2.

Let us consider in concluding this section the behaviour of the heat capacity on the critical isochore $\omega = 0$ in the vicinity of the critical point. Above the critical point we have (see Sec. 12)

$$U = U_{id} - \frac{a}{V},$$

whence we find for the heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ that

$$C_V = C_{V_{id}} \quad (T > T_{cr}). \tag{77.9}$$

Below the critical point we deal with a two-phase system and

$$U = xU_2 + (1-x)U_1 = U_{id} - \frac{xa}{V_2} - \frac{(1-x)a}{V_1}, \tag{77.10}$$

According to the lever rule (see Sec. 12), on the critical isotherm the fraction of the vapour-phase in the system is

$$\frac{x}{1-x} = \frac{V_{cr}-V_1}{V_2-V_{cr}} = -\frac{\omega_1}{\omega_2} = 1, \quad x = \frac{1}{2},$$

from which it follows that below the critical point

$$U = U_{id} - \frac{a}{2V_{cr}}\left[\frac{1}{1+\omega} + \frac{1}{1-\omega}\right] = U_{id} - \frac{a}{V_{cr}}\frac{1}{1-\omega^2}. \tag{77.11}$$

Using the third formula of (77.2), for the heat capacity we obtain

$$C_V = C_{V_{id}} + \frac{2a}{V_{cr}T_{cr}}\frac{\omega}{(1-\omega^2)^2}\frac{d\omega}{d\tau}. \tag{77.12}$$

Substituting the values of V_{cr} and T_{cr} and using the expression (77.7) for ω, we finally find

$$C_V = C_{V_{id}} + \frac{9}{2}N_A\frac{1}{(1-4\tau)^2} \approx C_{V_{id}} + \frac{9}{2}N_A. \tag{77.13}$$

Thus, the heat capacity of a van der Waals gas undergoes at the critical point a finite discontinuity jump

$$[C_V]_{T_{cr}} = C_V(T_{cr}+0) - C_V(T_{cr}-0) = -\frac{9}{2}N_A, \tag{77.14}$$

and the critical exponent α' is equal to zero.

Thus, we found that $\alpha' = 0$, $\beta = 1/2$, $\gamma' = 1$ and, consequently, $\alpha' + 2\beta + \gamma' = 2$, i.e. in a model of a van der Waals gas the Rushbrooke-Coopersmith inequality (76.10) degenerates into an equality. It is exactly the case with the Griffith inequality, and the same situation will be shown below to be encountered in other models.

As was shown in Secs. 12 and 65, the classical derivation of the van der Waals equation is based on the assumption of the short-range nature of intermolecular forces. M. Kac [27] has shown (considering a one-dimensional gas by way of example) that this equation can be derived on the basis of the diametrically opposite assumption that the range of molecular forces is infinitely large. In this case the humps and valleys on the van der Waals isotherms are automatically replaced by the isotherms satisfying Maxwell's equal-area rule. Kac substantiated this rather unexpected result with p[illegible]

sible (but not very rigorous) reasonings, showing the result to be apparently valid in the case of a three-dimensional gas as well.

Since the Kac theory is fairly complicated, we shall limit ourselves to the consideration of a rather simple derivation of the van der Waals equation based on the replacement of particle interaction by a self-consistent field, in which particles move independently from one another. This single-particle field $\mathcal{U}(\mathbf{r})$ is such that for each particle there exists a "forbidden" volume V_0, into which it cannot penetrate [$\mathcal{U}(\mathbf{r}) = \infty$ at $\mathbf{r} \in V_0$]. This volume is, naturally, assumed to be proportional to the total number of particles N, $V_0 = Nb$. When a particle is confined within an accessible volume $V - Nb$, it is acted upon by the long-range attraction forces with a potential $u = \text{const}$, assumed to be proportional to particle density, $u = -a(N/V)$. The expression for a single-particle integral of states is as follows:

$$Z = f(T) \int\limits_{V-Nb} e^{aN/VT}\, d^3r = f(T)\,(V - Nb)\, e^{aN/VT}, \quad (77.15)$$

where $f(T)$ is the factor appearing when integration is carried out over momenta. For the pressure we obtain from (77.15) the expression

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = NT\frac{\partial}{\partial V}(\ln Z)_T = NT\frac{\partial}{\partial V}\left[\ln(V - Nb) + \frac{aN}{VT}\right],$$

leading to the van der Waals equation

$$P = \frac{NT}{V - Nb} - \frac{aN^2}{V^2}.$$

Problems

1. Show that in the vicinity of the critical point the heat of phase transition $\lambda = \frac{16a}{9b}\sqrt{\tau} = 6N_A T_{cr}\sqrt{\tau}$.
2. Show that at $T \ll T_{cr}$ the heat of phase transition tends to the value $\lambda = \frac{a}{b} = \frac{27}{8} N_A T_{cr}$.

78. Phase Transition in Ferromagnetic Materials. Molecular Field Method and the Bragg-Williams Approximation

In Sec. 51 the behaviour of a system of non-interacting magnetic moments has been considered, and we have drawn the conclusion that such a system possesses only paramagnetic properties and magnetization is defined by the formula

$$\frac{M}{M_0} = L\left(\frac{\mu_B H}{T}\right), \quad (78.1)$$

where L (we omit the subscript j for the sake of brevity) is one of Langevin's quantum functions depending on particle's spin (or at $j \to \infty$ the classical Langevin function).

The assumption about the absence of interaction is invalid for ferromagnetic materials. Experimental studies have shown ferromagnetics to be capable of spontaneous magnetization in the absence of an applied field, and even in weak fields the magnetization reaches saturation. These properties are indicative of the fact that the orientation of magnetic moments in ferromagnetics is caused not so much by the applied field as by some internal orienting field, which is stronger than the applied field H, and is associated with the interaction of atomic magnetic moments. This hypothesis was suggested by Weiss, assuming the internal field to be proportional to the already existing magnetization

$$H_{\text{in}} = \gamma M, \tag{78.2}$$

where γ is the dimensionless *Weiss constant* depending on a substance and having very large values ($\gamma \sim 10^4$).

From the physical viewpoint this assumption is clearly substantiated as follows: an internal, or molecular, field originates only in a previously magnetized medium in which there already exists a preferred direction of the magnetic moments of particles. It is natural to assume in a first approximation the dependence of H_{ap} on M to be linear. This hypothesis is more exactly substantiated in the quantum-mechanical theory of ferromagnetism, in which the internal field manifests itself as the result of action of the so-called *exchange forces* [28].

Accepting the Weiss hypothesis, we must replace on the right hand side of Eq. (78.1) the applied field H by an effective field H_{ef}

$$H_{\text{ef}} = H + H_{\text{ap}} = H + \gamma M.$$

Then, we obtain the equation

$$\frac{M}{M_0} = L\left[\frac{\mu_B (H + \gamma M)}{T}\right]. \tag{78.3}$$

In particular, for a system of bosons with spin $s = 1/2$ this equation acquires the following form:

$$\frac{M}{M_0} = \tanh\left[\frac{\mu_B (H + \gamma M)}{T}\right]. \tag{78.4}$$

An exact solution of Eq. (78.4) is impossible, and we turn to the graphical method, writing it down in a parametric form. We denote the argument of Langevin's function by x:

$$\frac{\mu_B (H + \gamma M)}{T} = x. \tag{78.5}$$

Then Eq. (78.4) can be presented as a system of two equations containing the parameter x:

$$\frac{M}{M_0} = \tanh x, \quad \frac{M}{M_0} = \frac{T}{\gamma M_0 \mu_B} x - \frac{H}{\gamma M_0}. \tag{78.6}$$

On the M/M_0-x diagram, shown in Fig. 102, the first of the two equations is presented by the curve $\tanh x$, and the second by the straight line, cutting off on the ordinate axis the segment $-\frac{H}{\gamma M_0}$, whose slope to the x-axis is determined by the formula

$$\tan \varphi = \frac{T}{\gamma M_0 \mu_B}. \tag{78.7}$$

It is clear from Fig. 102 that in the presence of an applied field, i.e. when $H \neq 0$, the Langevin curve $\tanh x$ and the straight line (78.6) never intersect at origin of coordinates and, consequently, there exists a magnetization M differing from zero. The behaviour of the intersection point as $H \to 0$ essentially depends on the angle of inclination of the straight line and, consequently, on temperature.

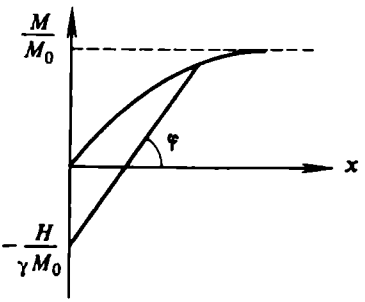


FIG. 102

The cases when the angle φ is larger or smaller than the angle between the tangent to the curve $\tanh x$ at the origin of coordinates and the x-axis should be considered separately. These two cases are characterized respectively by the inequalities

$$\frac{T}{\gamma M_0 \mu_B} > 1, \quad \frac{T}{\gamma M_0 \mu_B} < 1.$$

Let us introduce the quantity T_C, having the dimension of temperature (Curie's temperature) and specified by formula

$$T_C = \gamma M_0 \mu_B. \tag{78.8}$$

In the case when $T < T_C$, the straight line described by Eq. (78.6) intersects at the limit $H \to 0$ the Langevin curve at the point with the ordinate $M/M_0 \neq 0$ (Fig. 103) and, consequently, the specimen investigated possesses spontaneous magnetization, which is the closer to saturation magnetization M_0 the lower the temperature. Since only ferromagnetic materials possess spontaneous magnetization, this means that at $T < T_C$ the substance is in the ferromagnetic state.

At $T > T_C$ the straight line in (78.6) at $H \to 0$ intersects the Langevin curve only at the origin of coordinates (Fig. 104) and consequently, spontaneous magnetization is absent, $M = 0$. Since this property is characteristic of paramagnetic materials, at $T > T_C$ the substance is in the paramagnetic state.

Thus, the Curie point is the temperature at which a transition from the ferromagnetic state to the paramagnetic state takes place, or vice versa. From the physical viewpoint this should be interpreted as follows: at the Curie point the thermal motion of atoms becomes

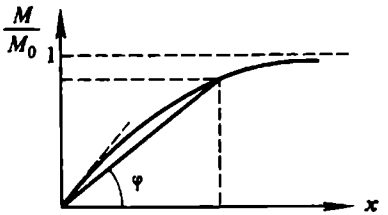


FIG. 103

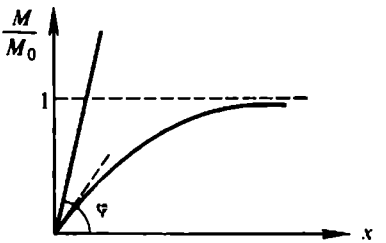


FIG. 104

so intensive that it compensates for the orienting action of the Weiss internal field. At higher temperatures the only non-compensated orienting factor is the applied field, which is the characteristic property of paramagnetics.

Equation (78.4) is merely the equation of state and, consequently, it does not make it possible to construct the complete thermodynamics of ferromagnetics, for which purpose, as has been shown in Sec. 14, the knowledge of any thermodynamic potential is necessary.

Let us consider in this connection one more approximate solution method for the problem, known as the *Bragg-Williams method*. (This can also be used to solve other problems in physics (see the problems to this section). This method will be shown below to lead to the same equation of state (78.4), but it in addition permits to express the temperature T_C in terms of some characteristic parameters of the crystal lattice and construct the complete thermodynamics of the lattice.

Let us consider a crystal lattice of some arbitrary dimension (linear, plane, spatial) and arbitrary symmetry, in the fixed sites of which particles are located with spin $s = 1/2$, and magnetic moment μ_B. We denote the coordination number of the lattice considered by n, i.e. the number of the closest neighbours for each fixed site (for a line lattice $n = 2$, for a flat lattice composed of regular triangles $n = 6$, etc.). Let N_+ and N_- denote the number of particles having magnetic moments parallel to the field and antiparallel to the field

respectively, $N_+ + N_- = N$. Let us introduce the long-range order parameter X specified by this formula

$$X = \frac{N_+ - N_-}{N} = \frac{M}{M_0}. \tag{78.9}$$

The name "long-range parameter" is associated with the fact that the quantity X only indicates the degree of prevailance in the lattice of particles with magnetic moments parallel to the field, but it tells us nothing concerning the correlation in the directions of neighbouring spins, i.e. of the short-range order.

Expressing N_+ and N_- in terms of X, we obtain

$$\frac{N_+}{N} = \frac{1}{2}(1+X), \quad \frac{N_-}{N} = \frac{1}{2}(1-X). \tag{78.10}$$

Further reasonings are based on two simplifying assumptions, of which the first consists in that the interaction forces are assumed to be of the short-range kind, so that only the closest neighbours interact with each other in the lattice. Let the energy of interaction between two neighbouring particles with similarly directed spins be equal to ε, and the energy of interaction between particles with oppositely directed spins be equal to ε. Only the case with $\varepsilon > 0$ will be considered below, i.e. a system tending to magnetic ordering. Then, the oriented fraction of the internal energy, including the energy of the moments μ_B in the magnetic field, will be expressed by formula

$$U = (N_{+-} - N_{++} - N_{--})\varepsilon - (N_+ - N_-)\mu_B H, \tag{78.11}$$

where N_{++}, N_{--}, N_{+-} are the number of pairs of closest neighbours with spins parallel to the field, antiparallel to the field and oppositely directed spin respectively.

Let us introduce now the second essential assumption of the Bragg-Williams method. In the course of computation it is assumed that there is no short-range order in the system, i.e. there is no correlation between the directions of spins of neighbouring particles, with the exception of that imposed on the system by the long-range order existing in it. In other words, any direction of a spin, adjacent to a spin directed parallel to the field, for instance, will be considered equiprobable, although, actually, due to the fact that $\varepsilon > 0$, there exists a tendency to parallel ordering of spins of neighbouring particles. In the Bragg-Williams method the short-range order originates only as a result of the minimization of free energy (see below), but it is not envisaged in the initial assumptions.

Let us introduce alongside with the long-range parameter X the short-range order parameter Y, defining it as the ratio of the difference $N_{++} + N_{--} - N_{+-}$ to the total number of closest neighbours in the lattice,

$$Y = \frac{N_{++} + N_{--} - N_{+-}}{1/2\, nN}$$

and leave it to the reader to prove that in the Bragg-Williams approximation Y is a function of X, $Y = X^2$. We calculate the numbers N_{++}, N_{--}, N_{+-}, departing from the basic hypothesis. To calculate N_{++}, for instance, we sort out all N_+ particles with the moment in the direction of the field and take into account, ignoring the correlations, that the average number of its neighbours with moments in the same direction is equal to nN_+/N. Since in doing so each pair is accounted for twice, the result must be divided by two. So, using formula (78.10), we obtain

$$N_{++} = N_+ \frac{1}{2} n \frac{N_+}{N} = \frac{nN}{8}(1+X)^2,$$
$$N_{--} = \frac{nN}{8}(1-X)^2, \quad N_{+-} = \frac{nN}{4}(1-X^2), \tag{78.12}$$

and the expression for the orientation energy becomes

$$U(X) = -\frac{nN\varepsilon}{2} X^2 - N\mu_B HX. \tag{78.13}$$

Let us calculate the entropy in the same assumption. Assuming all spin configurations to be equiprobable, according to the Boltzmann equation and using Stirling's formula, we have

$$S = \ln\left(\frac{N!}{N_+!\,N_-!}\right) = N\ln N - N_+ \ln N_+ - N_- \ln N_-.$$

Expressing N_+ and N_- in terms of X, in accordance with formula (78.10), we find that

$$S = -\frac{N}{2}\left[(1+X)\ln\frac{1+X}{2} + (1-X)\ln\frac{1-X}{2}\right],$$

whence for the free energy $F = U - TS$ we obtain

$$F(T, X) = -\frac{Nn\varepsilon}{2} X^2 - N\mu_B HX + \frac{NT}{2}\left[(1+X)\ln\frac{1+X}{2} + (1-X)\ln\frac{1-X}{2}\right].$$

In equilibrium F, being a function of X, must assume a minimum value, and from this condition we find the equation

$$\left(\frac{\partial F}{\partial X}\right)_T = -N\left[n\varepsilon X + \mu_B H - \frac{T}{2}\ln\frac{1+X}{1-X}\right] = 0, \tag{78.14}$$

which can easily be transformed into

$$X = \tanh\left(\frac{\mu_B H + n\varepsilon X}{T}\right) = \tanh\left(\frac{T_{cr}}{T} X + \frac{\mu_B H}{T}\right), \tag{78.15}$$

which is fully equivalent to formula (78.4). Comparing these equations, we find the expression for the Weiss coefficient

$$\gamma = \frac{n\varepsilon}{M_0\mu_B} = \frac{n\varepsilon}{N\mu_B^2}.$$

At $H = 0$ Eq. (78.15) was seen above to have a nonzero solution only at $T < T_{cr}$, where the transition temperature T_{cr} is expressed by

$$T_{cr} = \gamma M_0 \mu_B = n\varepsilon, \tag{78.16}$$

and at $T \geqslant T_{cr}$, $X = 0$. The reader is to make sure that at $T < T_{cr}$ of the two roots of Eq. (78.15) it is exactly the root $X \neq 0$ that corresponds to the minimum of free energy.

Let us examine now the thermodynamic behaviour of a magnetic material in the vicinity of the phase-transition point and find, in particular, the critical indices (exponents) considering first spontaneous magnetization and assuming $H = 0$ Eq. (78.15) acquires the form

$$X = \tanh\left(\frac{T_{cr}}{T} X\right). \tag{78.17}$$

At $T \to T_{cr} - 0$, the quantity X is small compared with unity and $\tanh\left(\frac{T_{cr}}{T} X\right)$ can be expanded into a Taylor series, preserving the two first terms of the expansion:

$$\tanh\left(\frac{T_{cr}}{T} X\right) = \frac{T_{cr}}{T} X - \frac{1}{3}\left(\frac{T_{cr}}{T} X\right)^3 + \ldots .$$

Substituting this expansion into (78.17), we obtain

$$\left(1 - \frac{T_{cr}}{T}\right) X + \frac{1}{3}\left(\frac{T_{cr}}{T}\right)^3 X^3 = 0.$$

The nonzero root of this equation is equal to

$$X = (3\tau)^{1/2},$$

accurate to the first-order infinitesimals in $\tau = (T_{cr} - T)/T_{cr}$, i.e. in the Bragg-Williams approximation the exponent $\beta = 1/2$.

Let us also find the critical index δ. At $H \to 0$ and $T \to T_{cr}$, the argument of the hyperbolic tangent in (78.15) is small. Expanding it into a series in powers of the argument and preserving only the lower powers of X and $\mu_B H/T$, we find

$$X\left(\frac{T_{cr}}{T} - 1\right) + \frac{\mu_B H}{T} - \frac{1}{3}\left(\frac{T_{cr}}{T}\right)^3 X^3 = 0, \tag{78.18}$$

from which it follows that at $T \to T_{cr}$ we have

$$\frac{\mu_B H}{T} = \frac{X^3}{3}, \tag{78.19}$$

i.e. the critical exponent $\delta = 3$. To find the magnetic susceptibility $\chi = \left(\frac{\partial M}{\partial H}\right)_T = M_0\left(\frac{\partial X}{\partial H}\right)_T$, we differentiate Eq. (78.15) with

respect to H, and assuming then $H = 0$, we find

$$\chi_m = \frac{M_0\mu_B/T}{\cosh^2\left(\frac{T_{cr}}{T}X\right) - \frac{T_{cr}}{T}}. \tag{78.20}$$

At $T \geqslant T_{cr}$, $X = 0$ and from formula (78.20) we obtain $\chi_m = -M_0\mu_B/T_{cr}\tau$. At $0 < (T_{cr} - T)/T_{cr} \ll 1$, expanding $\cosh^2\left(\frac{T_{cr}X}{T}\right)$ and using formula (78.18), we find

$$\cosh^2\left(\frac{T_{cr}X}{T}\right) = 1 + \frac{1}{2}\left(\frac{T_{cr}X}{T}\right)^2 \approx 1 + \frac{3}{2}\tau,$$

whence

$$\chi_m = \frac{2M_0\mu_B}{T_{cr}\tau}.$$

Thus, in the Bragg-Williams approximation the indices γ and γ' are the same and equal to unity, $\gamma = \gamma' = 1$, but the susceptibility in the ferromagnetic region ($\tau > 0$) is twice as large as in the paramagnetic region at the same $|\tau|$.

Let us consider, finally, the behaviour of the heat capacity C_H in the vicinity of the critical point. According to formula (78.13), at $H = 0$ we have

$$U(X) = -\frac{NT_{cr}}{2}X^2,$$

whence

$$C|_{H=0} = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial X}\frac{dX}{dT} = -NT_{cr}X\frac{dX}{dT} = NX\frac{dX}{d\tau}. \tag{78.21}$$

From formula (78.21) it follows that at $T \geqslant T_{cr}$, $X = 0$ and $C|_{H=0} = 0$, and at $T < T_{cr}$, using formula (78.18), we find $C|_{H=0} = \frac{3}{2}N$, correct to infinitesimals of the order of τ. Thus, the orientation heat capacity has at the critical point $T = T_{cr}$ a simple discontinuity jump

$$[C] = C(T_{cr} + 0) - C(T_{cr} - 0) = -\frac{3}{2}N,$$

and the two critical indices α and α' are equal to zero.

All critical indices in the Bragg-Williams approximation were shown to coincide with the values obtained for them in the theory of the van der Waals gas. From this it follows, in particular, that the Rushbrooke-Coopersmith and Griffith inequalities (76.11) and (76.12) degenerate into equalities.

In concluding the section it is useful to make the following remarks. One of the assumptions made in deriving the equation of a self-consistent field (78.15) was that only closest neighbours interact in a lattice, i.e. that the interaction forces are of the short-range kind.

As was found later [26], this assumption was not essential and, moreover, it turned out, just as in the case of the van der Waals equation (see the end of Sec. 77), that the equation of state (78.15) could be derived from only one assumption (without the second Bragg-Williams hypothesis) stating that all lattice spins, both the neighbouring and non-adjacent, interact equally strongly with each other (the proof is given, for instance in [26]). It should, however, be noted that considered in [26] is infinite-range ($r_0 \propto N$), but infinitely weak interaction ($\mathcal{U} \propto N^{-1}$) and the above result is valid in the peculiar thermodynamic limit ($N \to \infty$, $r_0 \to \infty$, $\mathcal{U} \to 0$, the product $\mathcal{U}N$ is finite).

Thus, the two "classical" theories, the van der Waals theory of a real gas and the Weiss-Bragg-Williams ferromagnetic theory, proved ratherunexpectedly to be valid in the limit of "long-range" interactions.

Problems

1. Find the solution of the equation $X = \tanh\left(\frac{T_{cr}}{T} X\right)$ and the heat capacity at $T/T_{cr} \ll 1$.
2. Prove that in the Bragg-Williams approximation the short-range order parameter Y is related with the long-range order parameter X by the formula $Y = X^2$.
3. Making use of the Bragg-Williams approximation, consider an ordered alloy AB. In a lattice with a coordination number n there are $N/2$ fixed sites of each of the a- and b-types. At absolute zero ions A occupy the a-type fixed sites, and ions B are arranged at the b-type fixed sites of the lattice. At $T > 0$ the transition to "alien" lattice sites begins. Denoting respectively by N_{Aa}, N_{Ab}, and N_{Bb}, N_{Ba} the number of ions occupying the "proper" and "alien" sites in the lattice,

$$N_{Aa} + N_{Ab} = N_{Bb} + N_{Ba} = \frac{N}{2}, \quad N_{Aa} + N_{Ba} = N_{Ab} + N_{Bb} = \frac{N}{2},$$

and using the notation $X = \frac{N_{Aa} - N_{Ab}}{N/2}$ for the long-range parameter and ε_{AA}, ε_{BB} and ε_{AB} for the energy of interaction between ion pairs AA, BB, AB $\left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} > \varepsilon_{AB}\right)$: (a) find the equation for X; (b) solve this equation in the region $0 < \tau \ll 1$ and in the region $T/T_{cr} \ll 1$, and also determine T_{cr}; (c) find the heat capacity in the same temperature regions. The nearest neighbours are assumed to be only the fixed sites of different sublattices a and b.

79. The Landau Theory of Second-Order Phase Transitions

L. D. Landau has created a rather general theory of second-order phase transitions [18], based on the following assumptions.

1. The physical system in question can be characterized, in addition to the ordinary physical parameters P, V, T, H, etc., also by the long-range order parameter X, depending on the selection of the system. In the problem involving magnetic materials the role of this parameter can be played by the relative or absolute magnetization, M/M_0 or M; in a problem concerning an ordered binary alloy (see problem 3 to Sec. 78) the quantity $X = \frac{N_{Aa} - N_{Ab}}{N/2}$ is the relative difference in the number of ions occupying "proper" and "alien" fixed sites, etc.

2. Close to the phase-transition point T_{cr}, at which the parameter X becomes zero, the thermodynamic potentials can be expanded into a power series in X, with the terms of the expansion used in computations being sufficiently small and having no peculiarities. This assumption permits one to derive equations determining the parameter X as a function of pressure and temperature, and construct the thermodynamics of the system. We shall consider the Landau theory as applied to a ferromagnetic material.

Let us consider a ferromagnetic material as a system with two mechanical degrees of freedom: coordinates—molar volume $\tilde{V}$ and molar magnetization M; "forces"—pressure P and the magnetic field intensity H taken with the opposite sign. Then, by analogy with formula (22.9), the chemical potential μ is expressed by

$$\mu = \tilde{U}^* - T\tilde{S} + P\tilde{V} - HM, \quad d\mu = -\tilde{S}\,dT + \tilde{V}\,dP - M\,dH, \tag{79.1}$$

where μ, $\tilde{S}$, $\tilde{V}$, M must be regarded as functions of the variables T, P and H.

Let us use the Legendre transformation to shift from the variables M and H to the variables T, P, M, by introducing the potential $\tilde{\mu} = \mu + MH$:

$$d\tilde{\mu}\,(T, P, M) = -\tilde{S}\,dT + \tilde{V}\,dP + H\,dM \tag{79.2}$$

In accordance with the basic assumption of Landau's theory, the potential $\tilde{\mu}\,(T, P, M)$ can be expanded near the phase-transition points into a power series in M. We shall consider an isotropic model of the ferromagnetic material, so that the opposite directions of magnetization, M and $-M$, are physically equivalent, and the expansion is performed in even powers of M. Limiting ourselves to

three terms, we have

$$\mu = \tilde{\mu} - MH = \tilde{\mu}(T, P, 0) + \frac{\alpha(T, P)}{2} M^2 + \frac{\beta(T, P)}{4} M^4 - MH. \quad (79.3)$$

In thermodynamic equilibrium the chemical potential must have a minimum value and, consequently, at fixed T and P

$$\frac{\partial \mu}{\partial M} = 0, \quad \frac{\partial^2 \mu}{\partial M^2} > 0. \quad (79.4)$$

From this we obtain

$$M[\alpha(T, P) + \beta(T, P) M^2] - H = 0, \quad \alpha(T, P) + 3\beta(T, P) M^2 > 0. \quad (79.5)$$

It should be noted that the above relationships define magnetization M as a function of T, P, and H, $M = M(T, P, H)$; substituting this function into the expansion (79.3), we find the chemical potential as a function of the same variables.

Let us consider now the magnetic material with a switched off applied field, $H = 0$. Relationships (79.5) reduce to

$$M[\alpha(T, P) + \beta(T, P) M^2] = 0, \quad \alpha(T, P) + 3\beta(T, P) M^2 > 0. \quad (79.6)$$

Equation (79.6) has two roots $M = 0$, $M = \sqrt{-\frac{\alpha(T, P)}{\beta(T, P)}}$, with the inequality of (79.6) yielding $\alpha(T, P) > 0$ for the first root and $\alpha(T, P) < 0$, $\beta(T, P) > 0$ for the second root.

The paramagnetic state ($T > T_{cr}$) is associated with the root

$$M = 0, \quad \alpha(T, P) > 0; \quad (79.7)$$

the ferromagnetic state ($T < T_{cr}$) corresponds to the root

$$M = \sqrt{-\frac{\alpha(T, P)}{\beta(T, P)}}, \quad \alpha(T, P) < 0, \quad \beta(T, P) > 0. \quad (79.8)$$

At the Curie point the coefficient $\alpha(T, P)$ changes the sign and, therefore,

$$\alpha(T_{cr}, P_{cr}) = 0. \quad (79.9)$$

The equation obtained defines the phase-transition curve plotted on the P-T plane. It should be noted that the paramagnetic state is unstable at $\alpha(T, P) < 0$, $T < T_{cr}$, and the ferromagnetic state at $\alpha(T, P) > 0$, $T > T_{cr}$, for these values correspond to the maximum values of the chemical potential $\left(\frac{\partial^2 \mu}{\partial M^2}\right) < 0$ and not to the minimum values.

Close to the phase-transition point, where $\alpha(T_{cr}, P_{cr}) = 0$, the function $\alpha(T, P)$ can be expanded into a power series in (T —

$-T_{cr}$), retaining only the first linear term

$$\alpha(T, P) \quad \left(\frac{\partial \alpha}{\partial T}\right)_{cr}(T-T_{cr}). \tag{79.10}$$

where

$$\left(\frac{\partial \alpha}{\partial T}\right)_{cr}=\frac{\partial \alpha(T, P_{cr})}{\partial T}\Big|_{T=T_{cr}}>0.$$

Substituting this expression into (79.8), we find

$$M=\sqrt{\frac{(\partial \alpha/\partial T)_{cr}}{\beta_{cr}}}\sqrt{T_{cr}-T}, \tag{79.11}$$

showing that as the Curie point is approached, the spontaneous magnetization decreases in proportion to $\tau^{1/2}$ and the exponent β in the Landau theory is also equal to 1/2.

Let us calculate the chemical potential, the entropy and the volume of the magnetic material with the aid of expansion (79.5). Substituting into formula (79.3) the value of magnetization from (79.7) and (79.8) and assuming $H = 0$, we obtain:

in the paramagnetic domain

$$\mu_p=\tilde{\mu}(T, P, 0) \tag{79.12}$$

in the ferromagnetic domain

$$\mu_f=\tilde{\mu}(T, P, 0)-\frac{\alpha^2(T, P)}{4\beta(T, P)}. \tag{79.13}$$

Differentiating these expressions with respect to temperature, we obtain the expression for entropy:

in the paramagnetic domain

$$\tilde{S}_p=-\frac{\partial \tilde{\mu}(T, P, 0)}{\partial T}=S_0, \tag{79.14}$$

in the ferromagnetic domain

$$\tilde{S}_f=\tilde{S}_0+\frac{1}{4}\frac{\partial}{\partial T}\left(\frac{\alpha^2(T, P)}{\beta(T, P)}\right)=\tilde{S}_0+\frac{\alpha(2\alpha'_T\beta-\alpha\beta'_T)}{4\beta^2}. \tag{79.15}$$

Differentiating formulae (79.12) and (79.13) with respect to pressure, we find the expression for volume:

in the paramagnetic domain

$$\tilde{V}_p=\frac{\partial \tilde{\mu}(T, P, 0)}{\partial P}=\tilde{V}_0, \tag{79.16}$$

in the ferromagnetic domain

$$\tilde{V}_f=\tilde{V}_0-\frac{1}{4}\frac{\partial}{\partial P}\left(\frac{\alpha^2(T, P)}{\beta(T, P)}\right)=\tilde{V}_0-\frac{\alpha(2\alpha'_P\beta-\alpha\beta'_P)}{4\beta^2}. \tag{79.17}$$

Since at the Curie point the function $\alpha(T, P)$ becomes zero, it is clear from the two formulae that the discontinuity jumps in entropy and volume at the Curie point are equal to zero.

Let us calculate the discontinuity jumps in heat capacity and compressibility at the Curie point and show that they differ from zero, and that, consequently, the transition from the paramagnetic state to the ferromagnetic one at $H = 0$ is a second-order phase transition. We obtain

$$[C_P] = T_{cr} \frac{\partial}{\partial T} (\widetilde{S}_f - \widetilde{S}_p)|_{T_{cr}} = \frac{(\partial\alpha/\partial T)^2_{cr} T_{cr}}{\beta_{cr}}, \qquad (79.18)$$

and, since $\beta_{cr} > 0$, the heat capacity in the ferromagnetic state is larger than that in the paramagnetic state. Thus, according to the Landau theory, the heat capacity undergoes a finite discontinuity jump and α and α' vanish. Then, we find

$$\left[-\left(\frac{\partial \widetilde{V}}{\partial P}\right)_T\right] = \frac{(\partial\alpha/\partial P)^2_{cr}}{2\beta_{cr}}. \qquad (79.19)$$

and, consequently, the compressibility in the ferromagnetic state exceeds that in the paramagnetic state.

Finally, differentiating (79.16) and (79.17) with respect to temperature, we find the discontinuity jump in volume expansion

$$\left[\left(\frac{\partial V}{\partial T}\right)_P\right] = -\frac{\alpha'_T \alpha'_P}{2\beta}. \qquad (79.20)$$

Since the sign of α'_P is not specified theoretically (substances with α'_P have been shown experimentally to exist, the sign of the discontinuity jump $\left(\frac{\partial V}{\partial T}\right)_P$ is also undetermined. It is readily seen that the discontinuity jumps expressed by formulae (79.18) through (79.20) satisfy the Ehrenfest equation (28.4):

$$[C_P]\left[\left(\frac{\partial V}{\partial P}\right)_T\right] + T_{cr}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2 = 0.$$

Let us turn our attention to processes occurring in a magnetic material at $H \neq 0$. We must investigate a system of equations consisting of the cubic equation

$$M^3 + \frac{\alpha(T, P)}{\beta(T, P)} M - \frac{H}{\beta(T, P)} = 0 \qquad (79.21)$$

and the inequality

$$\alpha(T, P) + 3\beta(T, P) M^2 > 0. \qquad (79.22)$$

It is known (see, for instance, [29]) that Eq. (79.21) has one real root on condition

$$\frac{27}{4} H^2 > -\frac{\alpha^3}{\beta} \qquad (79.23)$$

and three real roots, if the opposite inequality

$$\frac{27}{4}H^2 \leqslant -\frac{\alpha^3}{\beta}. \tag{79.24}$$

is satisfied. In the first case the existence of only one phase of the substance is evidently possible, and it is clear from Eq. (79.21) that the magnetization in the region of weak fields [consistent, however, with formula (79.23)] is proportional to H. In fact, with weak fields the term M^3 in formula (79.21) can be ignored, whence $M \approx H/\alpha$; this root can be referred to as a paralike. With stronger fields magnetization is proportional to $H^{1/3}$, since the term αM can be ignored in Eq. (79.21) and $M \approx (H/\beta)^{1/3}$.

When inequality (79.24) is satisfied, α is for certain negative and it is convenient to introduce the quantity $\gamma(T, P) = -\alpha(T, P)$. Using the new notation, we rewrite expansion (79.3) and relationships (79.21) and (79.22) in the form

$$\mu = \tilde{\mu}(T, P, 0) - \frac{\gamma(T, P)}{2}M^2 + \frac{\beta(T, P)}{4}M^4 - MH, \tag{79.25}$$

$$M^3 - \frac{\gamma(T, P)}{\beta(T, P)}M - \frac{H}{\beta(T, P)} = 0, \tag{79.26}$$

$$3M^2 - \frac{\gamma(T, P)}{\beta(T, P)} > 0. \tag{79.27}$$

In this case Eq. (79.26) has three real roots expressed by [29]

$$M = 2\left(\frac{\gamma}{3\beta}\right)^{1/2}\cos\left(\varphi + \frac{2k\pi}{3}\right) \quad (k = 0, 1, 2), \tag{79.28}$$

where

$$\cos 3\varphi = \frac{3\sqrt{3}}{2}\frac{H\beta^{1/2}}{\gamma^{3/2}}, \quad 0 \leqslant \varphi \leqslant \frac{\pi}{6}. \tag{79.29}$$

Substituting (79.28) into the sufficient condition for expression (79.27) to be minimum, we obtain the inequality

$$\left|\cos\left(\varphi + \frac{2k\pi}{3}\right)\right| > \frac{1}{2},$$

which is satisfied at $k = 0$, 1, but fails to be true at $k = 2$. Thus, solutions with $k = 0$ and $k = 1$ correspond to minimum values of μ and a solution with $k = 2$ corresponds to the maximum value of μ and must be disregarded.

It remains to investigate which of the two solutions $k = 0$ or $k = 1$ corresponds to the absolute minimum and find out whether a phase transition may take place between the two phases complying with the two solutions. Substituting expression (79.28) with $k = 0$ or $k = 1$ into formula (79.25) and allowing for formula (79.29), we

obtain after some transformations

$$\mu|_{k=0} = \tilde{\mu}(T, P, 0) + \frac{\gamma^2}{6\beta}(1+\cos 2\varphi)(1-3\cos 2\varphi),$$

$$\mu|_{k=1} = \tilde{\mu}(T, P, 0) + \frac{\gamma^2}{6\beta}\left[1+\cos 2\left(\varphi+\frac{2\pi}{3}\right)\right] \times \left[1-3\cos 2\left(\varphi+\frac{2\pi}{3}\right)\right].$$

The reader can readily ascertain that the equation $\mu|_{k=0} = \mu|_{k=1}$ has no roots satisfying the condition $0 \leqslant \varphi \leqslant \pi/6$ and that the inequality $\mu|_{k=0} \leqslant \mu|_{k=1}$ exists (the equality is satisfied at $\varphi = \pi/6$ or $H^2 = \gamma^2/\beta$).

Thus, even when inequality (79.24) is satisfied, the stable state of only one phase is possible with $k = 0$, while states with $k = 1$ are possible only as metastable. It should be noted that at $k = 1$ magnetization is antiparallel to the applied field, $M < 0$.

The results of the above investigation of the states of a magnetic material at $H \neq 0$ can be comprehended with the aid of the following qualitative considerations. In the case of a paramagnetic state the dependence of the chemical potential on magnetization at $H = 0$ is represented by a curve with one minimum at $M = 0$ [the dotted curve in Fig. 105 (*a*)], and in the case of a ferromagnetic state, by a curve with two minima at $M = \pm\sqrt{\alpha/\beta}$ [Fig. 105 (*b*)]. When the magnetic field is applied, the term $-MH$ is added to the chemical potential, resulting in that the dependence of the chemical potential on magnetization changes [solid curves in Fig. 105 (*a*), (*b*)]. It is clear from Fig. 105 (*b*) that the right-hand minimum is deeper than the left-hand one. It should be noted that the solution with $k = 0$, $M = 2\left(\frac{\gamma}{3\beta}\right)^{1/2}\cos\varphi$ is of a "ferrolike" nature, i.e. magnetization weakly depends on H as φ changes from 0 to $\pi/6$. This corresponds, as is clear from formula (79.29), to the decrease in intensity from $\left(\frac{2\gamma^{3/2}}{3(3\beta)^{1/2}}\right)$

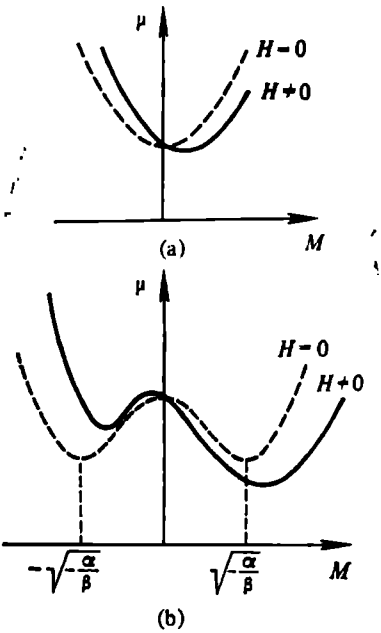


FIG. 105

to zero; at the same time magnetization diminishes only by a factor of $2/\sqrt{3}$.

Thus, at $H \neq 0$ the phase transition vanishes and is replaced by a continuous transition from the "ferrolike" behaviour of the ferromagnetic material to the "paralike" behaviour, as the parameter $H^2\beta/\gamma^3$ increases from values less than 4/27 to values greater than 4/27. It follows that in the H-T plane (P = const) there is an isolated point of the second-order phase transition, lying on the axis of abscissae. On the P-T plane ($H = 0$) we evidently have a second-order phase transition curve.

Let us find now the magnetic susceptibility of the magnetic material $\chi_m = \left(\frac{\partial M}{\partial H}\right)_{T,\,P}$. Differentiating (79.4) with respect to H, we obtain

$$\chi_m = \frac{1}{\alpha(T,\,P) + 3\beta(T,\,P)\,M^2}, \tag{79.30}$$

At $H = 0$ it follows from formula (79.30) that for the paramagnetic state $M = 0$, $\alpha(T,\,P) > 0$

$$\chi_m = \frac{1}{\alpha(T,\,P)},$$

while for the ferromagnetic state $M = \sqrt{-\alpha/\beta}$, $\alpha(T,\,P) < 0$

$$\chi_m = \frac{1}{2\alpha(T,\,P)}.$$

In the vicinity of the Curie point, where expansion (79.10) holds, these formulae acquire the form

$$\chi_m = \frac{1}{\left(\frac{\partial \alpha}{\partial T}\right)_{cr}(T - T_{cr})} \quad \text{at } T > T_{cr}, \tag{79.31}$$

$$\chi_m = \frac{1}{2\left(\frac{\partial \alpha}{\partial T}\right)_{cr}(T_{cr} - T)} \quad \text{at } T < T_{cr}. \tag{79.32}$$

In the case of weak magnetic fields $H \ll M/\chi_m \sim |\alpha|^{3/2}\beta^{1/2}$ Eqs. (79.31) and (79.32) can be integrated over H, which yields in the paramagnetic domain $T > T_{cr}$

$$M = \chi_m H \frac{H}{\left(\frac{\partial \alpha}{\partial T}\right)_{cr}(T - T_{cr})}, \tag{79.33}$$

in the ferromagnetic domain $T < T_{cr}$

$$M = \sqrt{-\frac{\alpha(T,\,P)}{\beta(T,\,P)}} + \frac{H}{2\left(\frac{\partial \alpha}{\partial T}\right)_{cr}(T_{cr} - T)}. \tag{79.34}$$

It should be noted that scope of application of the last two formulae is limited from both sides: the possibility of applying expansion (79.10) requires that temperature should be sufficiently close to the Curie point, but, on the other hand, at any fixed H the inequality

$$H \ll \frac{|\alpha|^{3/2}}{\beta^{1/2}} \propto \frac{(\partial\alpha/\partial T)_{cr}^{3/2} |T - T_{cr}|^{3/2}}{\beta_{cr}^{1/2}}$$

is violated at $|T - T_{cr}| \to 0$. It follows from here that the validity condition for formulae (79.33) and (79.34) is the inequality

$$\frac{H^{3/2}\beta_{cr}^{1/2}}{\left|\left(\frac{\partial\alpha}{\partial T}\right)_{cr}\right|} \ll \left|\frac{T - T_{cr}}{T_{cr}}\right| \ll \left|\frac{\left(\frac{\partial\alpha}{\partial T}\right)_{cr}}{\left(\frac{\partial^2\alpha}{\partial T^2}\right)_{cr} T_{cr}}\right|.$$

Relationships (79.31), (79.32) describe the *Curie-Weiss law* stating that the initial susceptibility and induced magnetization are inversely proportional to the quantity $|T - T_{cr}|$; consequently, the critical indices γ and γ' of the Landau theory coincide and are equal to unity, just as in the Bragg-Williams approximation and in the theory of the van der Waals gas. In this case the susceptibility and the induced magnetization in the ferromagnetic domain are twice smaller than in the paramagnetic domain at the same values of $|T - T_{cr}|$.

Let us now note the profound difference between second-order and first-order phase transition.

With first-order phase transitions, each phase is stable by itself on both sides of the transition point. This follows from the fact that both the chemical potential of the first phase $\mu_1(T, P)$ and the chemical potential of the second phase $\mu_2(T, P)$ are determined on both sides of the phase-transition point, and at a fixed temperature we can find the pressure corresponding to the minimum value of μ_i, and, on the contrary, at a fixed pressure find the temperature corresponding to the minimum value of μ_i for each phase. Such pressures and temperatures correspond to the equilibrium state of each phase on both sides of the phase-transition point. This follows from the fact that on the μ-P and μ-T diagrams (see Figs. 40, 41) the curves representing μ_1 and μ_2 exist on both sides of the intersection point, but one of them corresponds to the absolute minimum μ, i.e. to the absolutely equilibrium state—the curve with the smaller value of μ, and the other curve—the curve with the larger value of μ—corresponds to the minimum value for the given phase, i.e. to the metastable state of a substance. Accordingly, during first-order phase transitions superheating and supercooling phenomena are possible.

When a substance passes from the paramagnetic state to the ferromagnetic one at $H = 0$, i.e. upon a second-order phase transition,

the paramagnetic state $M = 0$ is absolutely unstable at $\alpha < 0$, $T < T_{cr}$, and the ferromagnetic state $M = \sqrt{-\alpha/\beta}$ is absolutely unstable at $\alpha > 0$, $T > T_{cr}$. The thermodynamic potential assumes in these cases a maximum value, $\frac{\partial^2 \mu}{\partial M^2} < 0$. This means that the chemical potential of the paramagnetic phase is not determined at all at $T < T_{cr}$, just as the chemical potential of the ferromagnetic state at $T > T_{cr}$. For this reason metastable states (superheating and supercooling) are impossible with second-order phase transitions.

This peculiarity of second-order phase transitions can also be understood proceeding from other, more graphical physical considerations. Since the chemical potential varies continuously at the phase transition point, there is a possibility of the appearance of a rather small quantity of a new phase whose properties differ strongly from the properties of the old phase, or of the appearance of a new phase in the entire volume of the substance, but with properties differing but little from the properties of the old phase.

The first case takes place during first-order phase transitions, when the new phase originates in small nuclei and has molar volume and molar entropy differing from the corresponding quantities of the old phase. In this case, as was shown in Sec. 27, the phase transition may be "delayed" due to the existence of surface energy, and metastable states appear.

The second case takes place during second-order phase transitions when a new phase, the phase with symmetry differing from that of the initial phase, appears at once in the entire volume and not in small "nuclei". Therefore no phase interface appears then between the phases and "delay" of phase transition is impossible.

With a second-order phase transition the dependence of the chemical potential on temperature and pressure is represented by a single smooth curve, and not by the intersection of two curves, as is the case with first-order phase transitions. It is clear, however, that the thermodynamic functions have some singularity on the phase transition line, if only because the second derivatives of the chemical potential undergo a discontinuity jump on that line. The nature of the singularity of the chemical potential on the line of second-order phase transitions is thus far not known. In this connection, the possibility of expanding the chemical potential into a power series in M^2 [formula (79.3)] is as a matter of fact problematic. Therefore all reasonings of this section are based on a so far non-verified hypothesis stating that the singularities of the chemical potential at phase transition points do not tell on the terms of the expansion of μ used in our mathematical computations. This fact was insistently emphasized by L.D. Landau—the author of the theory of second-order phase transitions.

Problem

Find the critical index δ in the Landau theory and check the Rushbrooke-Coopersmith and Griffith inequalities.
Answer. $\delta = 3$.

80. Review of Results. Comparison with Experiment. Models with Exact Solutions

We considered in Secs. 77 and 78 some approximate theories permitting the construction of thermodynamics in the vicinity of the phase-transition points: the van der Waals theory, the Bragg-Williams approximation, the Landau theory, all said to be classical.

All these theories lead to results disagreeing greatly with experimental results. It should be noted that as far as the predicted values of the critical exponents are concerned, these theories coincide in most cases. The exponent β, for instance, equal to 1/2 according to all theories considered, has been shown by experimental investigations to be closer to 1/3 (from 0.33 to 0.42) both for gas-liquid and magnetic systems. The classical theories set the exponents γ and γ' equal to 1, while, according to experimental data, they usually lie between 1.2 and 1.35. The exponent δ, that should be equal to 3 according to the classical theories, was shown experimentally to range between 4.2 and 4.4. Finally, although the exponents α and α' are shown by measurements to be rather small and possibly equal to zero in individual cases, experimental studies, however, are usually indicative not of a finite discontinuity jump in heat capacity at $T = T_{cr}$, but of a logarithmic divergence. A finite discontinuity jump is observed only when the heat capacity of each phase is determined over a finite, although small, distance from the Curie point on the temperature scale.

These contradictions are indicative of the fact that the classical theories are invalid exactly in the region for which they were elaborated. There is no wonder in this, however, since the prerequisites of the classical theories are rather rough idealizations of reality.

The probable reasons for the insufficiency of the Landau theory were discussed at the end of the preceding section. As regards the Bragg-Williams approximation, its basic assumption, the absence of close-range correlations, is undoubtedly even more rough. The insufficiency of this theory is confirmed additionally by the fact that in the Bragg-Williams theory a phase transition originates in any lattice irrespective of its spatial dimension and only the value of transition temperature T_{cr} depends on the coordination number n. It will be shown below that more exact methods reveal that no phase transitions take place in a unidimensional magnetic chain at any finite temperature.

It is, therefore, expedient to consider some models admitting *exact solutions*, i.e. such models for which the partition function of the Gibbs canonical or grand canonical distributions can be found without any approximation. Let us consider as an example of such a model the Ising unidimensional magnetic model, i.e. a unidimensional "crystal" with equidistantly spaced "fixed sites" (the total number of sites $N \gg 1$). Magnetic dipoles with a magnetic moment μ_B are arranged at the fixed sites of the lattice. The projection of the magnetic moment on the direction of the applied magnetic field // which is assumed to be permanent and homogeneous, can take two values, $\pm \mu_B$. Only neighbouring dipoles will be assumed interacting with each other, and the energies of interaction of two dipoles with the parallel and antiparallel magnetic moments will be denoted by ε and ε' respectively. In the case when $\varepsilon < \varepsilon'$ the parallel orientation of the moments is energetically more advantageous at $H = 0$, and when $\varepsilon > \varepsilon'$ the antiparallel orientation of adjacent dipoles is more beneficial.

The model described is known as the Ising model and it can, naturally, be specified for two- and three-dimensional cases.

Let us try to find the thermodynamic functions of a one-dimensional crystal. The partition function Z is expressed by

$$Z = \sum_{(C)} e^{-E(C)/T}, \tag{80.1}$$

where summation is performed over all configurations C, i.e. over all possible arrangements of dipoles of the first kind with a moment projection μ_B, and dipoles of the second kind with a moment projection $-\mu_B$ over the lattice fixed sites. Evidently, the total number of configurations is equal to 2^N. Let us introduce for each fixed site the variable σ_i, taking the value of 1 if the ith fixed site is occupied by a dipole of the first kind, and -1 if a second-kind dipole occupies this fixed site. The configuration is then determined by presetting all the numbers σ_i, assuming the lattice to be closed, i.e. the last fixed site is identified with the first: $\sigma_{N+1} = \sigma_1$. The energy of configurations $E(C)$ is expressed by the formula

$$E(C) = \sum_{i=1}^{N} \left[\frac{\varepsilon+\varepsilon'}{2} + \frac{\varepsilon-\varepsilon'}{2} \sigma_i \sigma_{i+1} - \frac{\mu_B H}{2} (\sigma_i + \sigma_{i+1}) \right]. \tag{80.2}$$

Introducing the notation

$$\rho(T) = \frac{\varepsilon+\varepsilon'}{2T}, \quad \theta(T) = \frac{\varepsilon'-\varepsilon}{2T}, \quad \tau(H, T) = \frac{\mu_B H}{2T}, \tag{80.3}$$

we can present the expression for Z in the form

$$Z = e^{-N\rho} \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} \exp[\theta\sigma_1\sigma_2 + \tau(\sigma_1+\sigma_2)] \exp[\theta\sigma_2\sigma_3 + \tau(\sigma_2+\sigma_3)] \times \ldots \times \exp[\theta\sigma_N\sigma_1 + \tau(\sigma_N+\sigma_1)]. \tag{80.4}$$

Let us introduce a two-row matrix $\hat{P}$ with matrix elements

$$P_{\sigma,\sigma'} = \exp[\theta\sigma\sigma' + \tau(\sigma+\sigma')], \tag{80.5}$$

$$\hat{P} = \begin{vmatrix} e^{\theta+2\tau} & e^{-\theta} \\ e^{-\theta} & e^{\theta-2\tau} \end{vmatrix}. \tag{80.6}$$

It can readily be seen that the sum in formula (80.4) is a spur of the Nth power of this matrix

$$Z = e^{-N\rho}\mathrm{Tr}\,(\hat{P}^N). \tag{80.7}$$

Since the trace (spur) of a matrix is invariant in respect to unitary similarity transformations, then reducing the matrix P to the diagonal form $\begin{vmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{vmatrix}$, we obtain from formula (80.7)

$$Z = e^{-N\rho}[\lambda_1^N + \lambda_2^N] = e^{-N\rho}\lambda_1^N\left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right] \approx e_1^{-N\rho}\lambda_1^N, \tag{80.8}$$

where λ_1 is the largest of the eigenvalues of matrix $\hat{P}$. The secular equation specifying the eigenvalues λ_1 and λ_2 is of the form

$$\begin{vmatrix} e^{\theta+2\tau}-\lambda & e^{-\theta} \\ e^{-\theta} & e^{\theta-2\tau}-\lambda \end{vmatrix} = \lambda^2 - 2e^{\theta}\cosh 2\tau\lambda + 2\sinh 2\theta = 0,$$

whence we find

$$\lambda_1 = e^{\theta}\cosh 2\tau + \sqrt{e^{2\theta}\cosh^2 2\tau - 2\sinh 2\theta}$$

$$= e^{\theta}\left[\cosh 2\tau + \sqrt{\sinh^2 2\tau + e^{-4\theta}}\right]. \tag{80.9}$$

It follows that the partition function is equal to

$$Z = e^{N(\theta-\rho)}\left[\cosh 2\tau + \sqrt{\sinh^2 2\tau + e^{-4\theta}}\right]^N. \tag{80.10}$$

Since the radicand in formula (80.10) is positive at any real τ and θ, the partition function Z and, consequently, all the thermodynamic functions are continuous at any temperature T and intensity H of the magnetic field. Therefore phase transitions are impossible in a unidimensional Ising model.

Using the formula $U = T^2\partial \ln Z/\partial T$ (see Sec. 63), we find the internal energy of the chain

$$U = N\left\{\varepsilon + 2T\frac{\theta e^{-4\theta} - \tau\sinh 2\tau\left[\cosh 2\tau + \sqrt{\sinh^2 2\tau + e^{-4\theta}}\right]}{\left[\cosh 2\tau + \sqrt{\sinh^2 2\tau + e^{-4\theta}}\right]\sqrt{\sinh^2 2\tau + e^{-4\theta}}}\right\}. \tag{80.11}$$

The expression for the heat capacity can be obtained from (80.11) by differentiating with respect to T; the computation is not presented here for it is rather involved. In the absence of a magnetic field ($\theta = 0$) the expression (80.11) simplifies considerably,

$$U|_{H=0} = N\left[\varepsilon + \frac{\theta T e^{-\theta}}{\cosh\theta}\right], \tag{80.12}$$

whence we find

$$C|_{H=0} = 2N\left(\frac{\theta}{\cosh\theta}\right)^2 = \frac{N}{2}\left\{\frac{\varepsilon-\varepsilon'}{T\cosh[(\varepsilon-\varepsilon')/2T]}\right\}^2. \quad (80.13)$$

The heat capacity tends to zero both as $T \to 0$ and as $T \to \infty$ and reaches its maximum value at the temperature $T_0 = |\varepsilon - \varepsilon'|/2\theta_0$, where θ_0 is the root of equation $\theta_0 = \coth\theta_0$. It should be noted that these results are true irrespective of the sign of $\varepsilon - \varepsilon'$.

Let us find the magnetization of the chain M. Substituting into the formula

$$M = \frac{\sum_{(C)}\sum_{j=1}^{N}\mu_0\sigma_j e^{-E(C)/T}}{Z} = \frac{1}{2}\mu_0\frac{\partial}{\partial\tau}(\ln Z) \quad (80.14)$$

the value of Z from (80.10), we find

$$M = M_0 \sinh 2\tau/\sqrt{\sinh^2 2\tau + e^{-4\theta}}, \quad (80.15)$$

where $M_0 = N\mu_0$ is the maximum magnetization.

Let us consider the limiting cases of high ($\theta \ll 1$, $\tau \ll 1$) and low ($\theta \gg 1$) temperatures.

I. The case when $T \to \infty$ or $H \to 0$. Then, $\tau \to 0$, $\theta \to 0$ and, according to (80.15), M also tends to zero. Since this corollary is true at any temperature, when $H = 0$, then in a unidimensional Ising chain ferromagnetism is impossible. From the physical viewpoint this is explained by the fact that with a small number of neighbours in a unidimensional chain (two nearest neighbours instead of four in a plane lattice) the tendency toward correlation in the position of adjacent magnetic moments is insufficient for the appearance of spontaneous magnetization.

II. The case when $T \to 0$. At this limit two cases must be examined separately: when $\theta > 0$ (there is a tendency toward a ferromagnetic ordering in the system) and $\theta < 0$ (there is a tendency toward antiparallel ordering).

$\theta > 0$. At $T \to 0$ we have $\theta \to \infty$, $\tau \to \infty$ and $M \to M_0$.

We have obtained a natural result: the most probable distribution of magnetic moments in a chain as $T \to 0$ is completely ordered and parallel to the field, and the magnetization is equal to its maximum value M_0.

$\theta < 0$. In this case to investigate the low-temperature region it is convenient, accounting for $\sinh 2\tau \approx \cosh 2\tau = 1/2e^{2\tau}$, to rewrite formula (80.15) to read

$$M = \frac{M_0}{\sqrt{1+4e^{4(|\theta|-\tau)}}}, \quad (80.16)$$

from which it follows that the behaviour of the chain with $\theta < 0$ at $T \to 0$ depends essentially on whether the inequality $|\theta| > \tau$ or the reverse inequality $|\theta| < \tau$ is satisfied.

Let $|\theta| > \tau$, $\varepsilon' < \varepsilon - \mu_B H$. This means that the magnetic field is so weak $[\tilde{H} < H_{cr} = (\varepsilon - \varepsilon')/\mu_B]$ that the antiparallel orientation of adjacent magnetic moments, that is more beneficial energetically in the absence of a field ($\varepsilon' < \varepsilon$), remains unchanged in the presence of a field as well. Then, as $T \to 0$ we have $e^{4(|\theta|-\tau)} \to \infty$ and we obtain from (80.16) that $M \to 0$. The most probable arrangement of magnetic dipoles is completely disordered.

Let now $|\theta| < \tau$, $\varepsilon - \mu_B H < \varepsilon' < \varepsilon$. This means that the magnetic field is so strong ($H > H_{cr} = \varepsilon - \varepsilon'/\mu_B$) that the antiparallel orientation of adjacent magnetic moments, which is more beneficial energetically in the absence of the field, becomes energetically less advantageous in the presence of the field. Then, as $T \to 0$, we have $e^{4(|\theta|-\tau)} \to 0$ and formula (80.16) yields $M \to M_0$. The most probable arrangement of magnetic moments is completely ordered and parallel to the field.

Thus, although no phase transition occurs in a one-dimensional Ising model, in the case of a chain with $\theta < 0$ there exists a critical magnetic field intensity $H_{cr} = (\varepsilon - \varepsilon')/\mu_B$ in the vicinity of which a transition takes place from a state with alternating dipoles of the first and of the second kind (at $H \ll H_{cr}$) to a completely ordered state (at $H \gg H_{cr}$), with the transition becoming abrupt at $T \to 0$.

The Ising model permits, in addition to the magnetic, other physical interpretations. Let us assume that each fixed site of a lattice can be occupied either by an atom of the A kind ($\sigma_i = 1$) or by an atom of the B kind ($\sigma_i = -1$), with only adjacent atoms interacting with each other. The one-dimensional chain is also assumed to be arranged in a solution containing a great number of atoms of the A and B kinds that can be adsorbed by the fixed sites of the chain, so that the numbers of atoms at the lattice sites, N_A and N_B, are not fixed and given is only their sum $N_A + N_B = N$. Following this interpretation we turn now to the already known binary alloy (one-dimensional). Let us denote by ε_{AA}, ε_{BB}, ε_{AB} the energy of interaction between two adjacent atoms of the A kind, two adjacent atoms of the B kind and the energy of interaction between an atom of the A kind and an atom of the B kind, respectively. Then, the energy of configuration $E(C)$ is expressed by

$$E(C) = \sum_{i=1}^{N} \left[\frac{\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}}{4} + \frac{\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB}}{4} \sigma_i \sigma_{i+1} + \frac{\varepsilon_{AA} - \varepsilon_{BB}}{4} (\sigma_i + \sigma_{i+1}) \right]. \quad (80.17)$$

Introducing the notations

$$p(T) = \frac{\varepsilon_{AA} + \varepsilon_{BB} + \varepsilon_{AB}}{4T},$$

$$\theta(T) = \frac{2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}}{4T}, \quad \tau(T) = \frac{\varepsilon_{BB} - \varepsilon_{AA}}{8T}, \quad (80.18)$$

we see that the problem concerning the properties of a binary one-dimensional chain is completely equivalent to the problem on the behaviour of a one-dimensional chain in a magnetic field, with the correspondance between the quantities characterizing the binary and magnetic chain being as follows:

$$\varepsilon \to \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}, \quad \varepsilon' \to \varepsilon_{AB}, \quad \mu_B H \to \frac{\varepsilon_{BB}-\varepsilon_{AA}}{4}$$

(without loss of generality we can assume $\varepsilon_{BB} > \varepsilon_{AA}$, so that the parameter τ, defined by formula (80.18), is positive, just as in the magnetic chain).

Let us assume that each of the N fixed sites of the lattice can be either occupied by one atom ($\sigma_i = 1$) or the fixed site can be vacant ($\sigma_i = -1$), and denote by $(-J)$ the energy of interaction between the atom occupying an arbitrary fixed site and its neighbour. We obtain, then, the already mentioned model of a lattice gas (one-dimensional). The energy of the configuration is expressed by the formula

$$E(C) = -\frac{J}{4}\sum_{i=1}^{N}[1+\sigma_i+\sigma_{i+1}+\sigma_i\sigma_{i+1}]. \qquad (80.1')$$

Introducing the notation $\rho(T) = -\frac{J}{4T}$, we obtain the expression for the partition function Z completely equivalent to formula (80.1') obtained above for a magnetic chain, if we denote anew $\varepsilon = -J$, $\varepsilon' = 0$, $\mu_B H = J/2$ [cf. (80.2) and (80.19)].

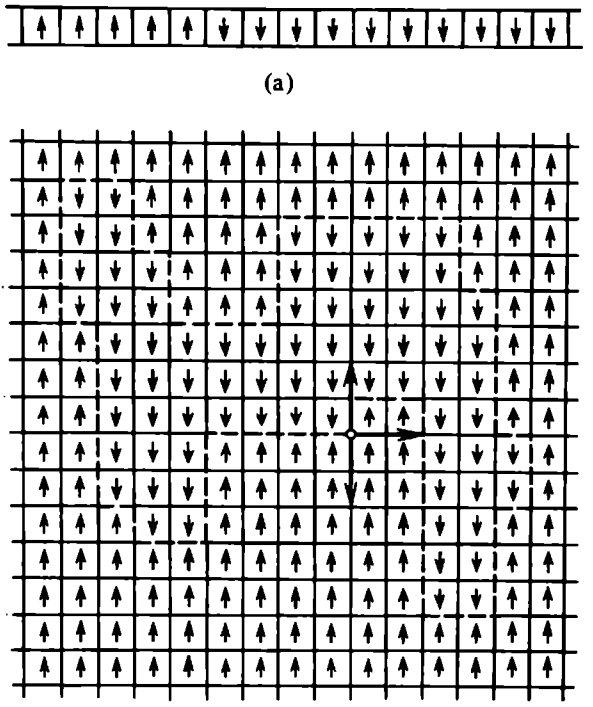
All the results pertaining to the distribution of A and B atoms in the binary chain and to the distribution of the atoms of a lattice gas can be obtained from the corresponding formulae for the Ising magnetic chain by means of simple transformations (see problem to this section).

Let us now carry out a simple qualitative reasoning showing that in a lattice with a number of spatial dimensions equal to or greater than two there exists a temperature below which spin ordering ($\varepsilon' > \varepsilon$) is thermodynamically beneficial, and that in a one-dimensional chain this temperature equals zero.

First let us consider a one-dimensional chain of spins ($s = 1/2$) in the absence of a magnetic field and compare its two states: the first state in which all spins have the same direction, and the second state in which all spins, beginning with a certain one, changed the direction to an opposite one [Fig. 106 (*a*)]. The energy of the second configuration is greater than that of the first by $\Delta U = \varepsilon' - \varepsilon$ (there appeared one pair of adjacent oppositely directed moments). Allowing for the fact that, according to the Boltzmann equation, the boundary between the oppositely directed spins can be chosen in N ways, the entropy of the second configuration exceeds that of the

must by ln N. It follows from this that the change in the free energy $\Delta F = \varepsilon' - \varepsilon - T \ln N$, so that at any $T \neq 0$ and macroscopic values of N, ΔF is negative and spin disordering is expedient thermodynamically.

Let us now consider a two-dimensional lattice and compare again two configurations—one with completely ordered moments and the other in which in the macroscopic subregion, shown in Fig. 106 (*b*) by the dotted line, the direction of the moments is reversed. Let us denote by N the number of links in the boundary between the two regions. Upon transition from the first configuration to the second



(a)

(b)

FIG. 106

the change in energy is equal to $N(\varepsilon' - \varepsilon)$. The number of ways in which the boundary of N links can be drawn is approximately equal to 3^N, since as long as we are positioned at a sufficiently large distance from the initial point A of the boundary, three possible directions exist for the next link, as shown in Fig. 106 (*b*). Consequently, the change in the free energy is expressed by $\Delta F = N[\varepsilon' - \varepsilon -$

$-T \ln 3]$, showing that at $T > T_{cr} = (\varepsilon' - \varepsilon)/\ln 3$ the quantity ΔF is positive and ordering of magnetic moments is beneficial thermodynamically. It is clear that this reasoning is also valid qualitatively for a three-dimensional lattice, and this explains the reason for the existence of phase transitions in ferromagnetic materials.

The Ising two-dimensional problem has an exact analytical solution at $H = 0$, although, rather complex and cumbersome. We shall limit ourselves to citing the main results and referring readers taking interest in the solution to the literature [18], [30], [31]. In a two-dimensional Ising model the phase transition temperature is determined by the relationship

$$T_{cr} = -\frac{\varepsilon' - \varepsilon}{\ln(\sqrt{2}-1)} = \frac{\varepsilon' - \varepsilon}{0.44}.$$

The heat capacity in the vicinity of the critical point (both above and below it) diverges logarithmically, $C \propto \ln |\tau|$, so that the critical exponents α and α' are equal to zero. Close to the critical temperature T_{cr} the spontaneous magnetization M changes following the law $M \propto \tau^{1/8}$, so that the exponent $\beta = 1/8$. The magnetic susceptibility diverges at the critical point, obeying the law $\chi_m \propto |\tau|^{-7/4}$, so that the exponent $\gamma = \gamma' = 7/4$. It is readily seen that in this case the Rushbrooke-Coopersmith inequality also degenerates into the equality $\alpha' + 2\beta + \gamma' = 2$. Finally, depending on $M \propto H^{1/\delta}$, the exponent δ can be estimated only approximately with the aid of numerical methods, and it is close to 15. Therefore in the Griffith inequality for the Ising two-dimensional model the equality $\alpha' + \beta(\delta + 1) \approx 2$ is satisfied with a good accuracy.

The Ising three-dimensional problem has not been solved analytically so far. Approximate estimates give the following values of the critical exponents: α and $\alpha' \sim 1/8$; $\beta \sim 5/16$, γ and $\gamma' \sim 5/4$ and $\delta \sim 5$; substitution of these exponents into the Rushbrooke-Coopersmith and Griffith inequalities transforms them into equalities.

Problems

1. Calculate the short-range order parameter $Y = \frac{N_{++} + N_{--} - N_{+-}}{1/2\, nN} = \frac{1}{N}\overline{\sum_i \sigma_i \sigma_{i+1}}$ in the Ising one-dimensional model and estimate its deviation from the value $Y = X^2$ in the Bragg-Williams approximation.

Answer. $Y = 1 - \dfrac{2e^{-4\theta}}{(\cosh 2\tau + \sqrt{\sinh^2 2\tau + e^{-4\theta}})\sqrt{\sinh^2 2\tau + e^{-4\theta}}}$

2. Find the internal energy, heat capacity and the long- and short-range order parameters for (a) a one-dimensional binary alloy and (b) a one-dimensional lattice gas.
3. The energy gap of a semiconductor depends on the electron density in the conduction band, obeying the law $\Delta = \Delta_0 - an$. Show that in such a material a first-order phase transition is possible and determine the phase transition temperature T_{cr} and the heat of phase transition (assume the effective masses of the electrons and holes to be the same and the valence band top to be fixed).

Answer. $T_{cr} = \left(\frac{\Delta_0}{f(0)\,aA}\right)^{2/3}$, $\lambda = -\frac{3\Delta_0/4}{1-1/2|f'(0)|\,[\Delta_0 a^2 A^2/f(0)]^{1/3}}$,

where $f(z) = \int_0^\infty \frac{x^{1/2}\,dx}{e^{x+z}+1}$, $f(0) = L_{1/2} = 0.673$, $A = 4\pi(2m/h^2)^{3/2}$.

The model is applicable provided $\Delta_0 a^2 < \left(\frac{2}{|f'(0)|}\right)^3 \frac{f(0)}{A^3}$.

4. Find the arrangement of the Q-sum zeros for a one-dimensional lattice gas. Investigate the thermodynamic limit.

Answer. On the complex plane of the variable $z = e^{\mu/T}$ the Q-sum zeroes are determined by relationship

$$z_n = e^{-\beta J}\left\{-1+2(1-e^{-\beta J})\cos^2\left(\frac{\theta_n}{2}\right) \pm 2i\sqrt{(1-e^{-\beta J})\cos^2\left(\frac{\theta_n}{2}\right)\left[1-(1-e^{-\beta J})\cos^2\left(\frac{\theta_n}{2}\right)\right]}\right\},$$

where $e^{i\theta_n}$ ($n = 0, 1, \ldots, [N/2]$) are the values of the Nth degree root of -1, $\theta_n = \pi(2n+1)/N$. The zeros lie on a circle of radius $e^{-\beta J}$ and do not get on the positive semi-axis even at the thermodynamic limit.

41. Fluctuations and Phase Transitions. The Ornstein-Zernike Theory. Similarity Hypothesis

Calculating the fluctuations in volume and density in Sec. 71, we found them to be proportional to compressibility $(\partial V/\partial P)_T$ and, consequently, the fluctuations increase infinitely as the critical point $[(\partial V/\partial P)_T \to \infty]$ is approached. It can be shown in the same way that the fluctuations in magnetization in a magnetic system, which are proportional to the magnetic susceptibility χ_m, also increase infinitely as the Curie point is approached. The reason for the anomalous increase in fluctuations in the vicinity of the phase-transition point is the weakened elastic properties of the system, the measure of which is the quantity $(\partial P/\partial V)_T$ in the case of a fluid and $(\partial H/\partial M)_T$ in the case of a magnetic system. For this reason the fluc-

tuations in fluid density or the fluctuations in the density of magnetization in a magnetic material in the vicinity of the phase-transition point correlate with each other at a large distances and embrace greater regions than far from the critical point. In experiments, this manifests itself in the anomalously strong scattering of electromagnetic waves—*critical opalescence*—and of the neutron flux by the fluid or a system of spins in a state close to the critical.

Let us consider the fluctuations in fluid density at a fixed total volume V and constant temperature. According to (72.1), the probability of fluctuation can be presented in the form

$$W \propto e^{-\Delta S} \sim e^{-\Delta F/T} \tag{81.1}$$

($\Delta U = 0$ at fixed V and T). Assuming density fluctuations to be small, ΔF is presented in the form

$$\Delta F = \int\int \frac{1}{2} d^3r\, d^3r' f(\mathbf{r} - \mathbf{r}') \Delta n(\mathbf{r}') \Delta n(\mathbf{r}). \tag{81.2}$$

There are no terms of the first order in $\Delta n(\mathbf{r})$ in this expansion, since, if fluctuations are ignored, the free energy must assume the minimum value. The second-order terms in (81.2) are assumed to be bilinear in $\Delta n(\mathbf{r})$ and not quadratic, meaning an allowance for the correlations between density fluctuations at different points. For a homogeneous isotropic liquid the function $f(\mathbf{r} - \mathbf{r}')$ depends only on $|\mathbf{r} - \mathbf{r}'|$ and differs markedly from zero only at distances smaller than the radius of action of molecular forces. Passing in (81.2) to integration over $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}'$ and $\mathbf{R} = (\mathbf{r} + \mathbf{r}')/2$, we obtain

$$\Delta F = \int\int d^3R\, d^3\rho\, f(\rho)\, \Delta n\left(\mathbf{R} + \frac{\boldsymbol{\rho}}{2}\right) \Delta n\left(\mathbf{R} - \frac{\boldsymbol{\rho}}{2}\right). \tag{81.3}$$

Taking into account the effective smallness of the term $\frac{\boldsymbol{\rho}}{2}$ in the arguments of the functions $\Delta n\left(\mathbf{R} \pm \frac{\boldsymbol{\rho}}{2}\right)$, let us expand these functions into a Taylor series

$$\Delta n\left(\mathbf{R} \pm \frac{\boldsymbol{\rho}}{2}\right) = \Delta n(\mathbf{R}) \pm \frac{1}{2} \nabla_i (\Delta n) \rho_i + \frac{1}{8} \nabla_i \nabla_k (\Delta n) \rho_i \rho_k, \tag{81.4}$$

whence we find for ΔF accurate to the second-order infinitesimals in ρ_i the expression

$$\Delta F = \int\int d^3R\, d^3\rho\, f(\rho) \left\{ [\Delta n(\mathbf{R})]^2 - \frac{1}{4} \nabla_i [\Delta n(\mathbf{R})] \nabla_k [\Delta n(\mathbf{R})] \rho_i \rho_k \right.$$
$$\left. + \frac{1}{4} \Delta n(\mathbf{R}) \nabla_i \nabla_k [\Delta n(\mathbf{R})] \rho_i \rho_k \right\}. \tag{81.5}$$

Transforming the integral taken over d^3R beginning with the third term on the right-hand side of (81.5) with the aid of the Gauss theo-

rom and ignoring the surface term that is of no interest to us, we get

$$\Delta F = \int\int d^3R\, d^3\rho\, f(\rho) \left\{ [\Delta n(\mathbf{R})]^2 - \frac{1}{2} \nabla_i [\Delta n(\mathbf{R})] \nabla_k [\Delta n(\mathbf{R})] \rho_i \rho_k \right\}$$

and integrating over ρ with the account of the isotropy of the function $f(\rho)$, we finally find

$$\Delta F = \int d^3R \left[\frac{a}{2} (\Delta n)^2 + \frac{b}{2} \nabla^2 (\Delta n) \right] = \int d^3R\, \Delta \mathcal{F}(\mathbf{R}), \qquad (81.6)$$

where

$$a = 2 \int f(\rho)\, d^3\rho, \quad b\delta_{ik} = -\int f(\rho)\, \rho_i \rho_k\, d^3\rho. \qquad (81.7)$$

The constant b in the above expressions is known to be positive, since the free energy assumes a minimum value at $n = \text{const}$, $\nabla(\Delta n) = 0$. Thus, for the free energy of unit volume $\Delta\mathcal{F}$ we have the representation

$$\Delta \mathcal{F} = \frac{a}{2} (\Delta n)^2 + \frac{b}{2} \nabla^2 (\Delta n).$$

It should be noted that the coefficient a in (81.6) has a simple physical meaning. Accounting for equality (22.9), $d\mu = -\tilde{S}\, dT + n^{-1}\, dP$ and the relationship $F = \tilde{F}n$, $dF_T = \left(\frac{P}{n} + \tilde{F} \right) dn = \mu dn$, we have

$$a = \left(\frac{\partial^2 \mathcal{F}}{\partial n^2} \right)_T = \left(\frac{\partial \mu}{\partial n} \right)_T = \frac{1}{n} \left(\frac{\partial P}{\partial n} \right)_T.$$

Since at the critical point $\left(\frac{\partial P}{\partial n} \right)_T = -\frac{N}{n^2} \left(\frac{\partial P}{\partial V} \right)_T$ vanishes, the coefficient a at the critical point vanishes too.

Let us find the equilibrium value of $\Delta n(\mathbf{R})$, using the fact that functional (81.6) must have a minimum value. For this problem Euler's equation acquires the form

$$\nabla^2 (\Delta n) - \frac{a}{b} \Delta n = 0. \qquad (81.8)$$

Let us find a spherically symmetrical solution of this equation, assuming the centre of fluctuation to be located at the point $r = 0$. We have (by analogy with Debye's equation in Sec. 66)

$$\Delta n(r) = \text{const}\, \frac{e^{-r/r_c}}{r}. \qquad (81.9)$$

The quantity r_c, referred to as the *correlation radius*, is equal to

$$r_c = \left(\frac{b}{a} \right)^{1/2}. \qquad (81.10)$$

Thus, far from the critical point density fluctuations decrease exponentially. As the critical point is approached, $a \to 0$, and the cor-

relation radius increases infinitely, with the density fluctuations decreasing much slower ($\propto r^{-1}$). The theory discussed above was suggested in a somewhat different form by Ornstein and Zernike and it is named after them.

In concluding this section let us examine briefly one more important trend in the theory of phase transitions, that found lately a wide development and is based on the so-called similarity hypothesis, or scaling (for greater detail see [26], [32], [33]).

Let us set forth the most visual introduction of the similarity hypothesis, considering a lattice of the Ising spins with an arbitrary dimension d (for a linear chain $d = 1$, for a plane chain $d = 2$, for a spatial chain $d = 3$). The Hamiltonian of this system is equal to

$$\mathscr{H} = -J \sum_{i,j} \sigma_i \sigma_j - \mu_B H \sum_i \sigma_i, \tag{81.11}$$

where summation in the first term is performed only over the closest neighbours. Close to the Curie point, T_{cr}, the correlation radius becomes rather large compared with the lattice constant or, in other words, large groups of magnetic moments are correlated with each other. This allows the following construction (Fig. 107 shows such construction for a plane lattice with $d = 2$). Let us combine groups of spins into "cells" having a linear dimension $\mathscr{L}l$, where $\mathscr{L} \gg 1$, but $\mathscr{L}l < r_c$. Each such cell contains $\mathscr{L}^d$ spins, and the number of cells in the lattice is equal to $N/\mathscr{L}^d$. Since a large group of cells is located in the region of correlated moments, it is natural to assume that inside a cell all moments are oriented in the same way, and moments of the cells behave as the moments of individual particles, i.e. they can point "up" or "down". Therefore, to each cell we can assign a variable θ_α ($\alpha = 1, 2, \ldots, N/\mathscr{L}^d$) taking, just as σ_i, the values ± 1 and assume that the Hamiltonian $\mathscr{H}$ can be expressed in terms of θ_α by a formula similar to (81.11), but with other parameters $\tilde{J}$ and $\mu_B \tilde{H}$:

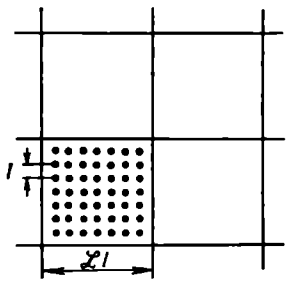


FIG. 107

$$\mathscr{H} = -\tilde{J} \sum_{\alpha,\beta} \theta_\alpha \theta_\beta - \mu_B \tilde{H} \sum_\alpha \theta_\alpha. \tag{81.12}$$

Since the quantity $\tilde{J}$ specifies the transition temperature T_{cr}, the transition from J to $\tilde{J}$ is equivalent to a change of the quantity $\tau = (T_{cr} - T)/T_{cr}$, which in the cell formalism becomes equal to

The similarity hypothesis consists of two assumptions. According to the first assumption, the thermodynamic functions in the model of cells and in the initial fixed-site model are similar to each other. For instance, for the Gibbs potential with natural variables τ and H we have the following relationship:

$$\Phi(\tilde{\tau}, \tilde{H}) = \mathcal{L}^d \Phi(\tau, H), \tag{81.13}$$

where $\Phi(\tilde{\tau}, \tilde{H})$ = Gibbs potential per one cell;
$\Phi(\tau, H)$ = Gibbs potential per one fixed site.

The second part of the hypothesis relates the parameters $\tilde{\tau}$ and τ and $\tilde{H}$ and H, which must be proportional to each other. This follows from the fact that the cell model is concerned with the same physical system, only in another mathematical formulation, and it must remain linear over the field and possess the same singularities as the critical point is approached. In these relationships the proportionality factors must depend on the similarity parameter $\mathcal{L}$. The simplest assumption made in the similarity hypothesis consists in that this dependence is assumed to be exponential with exponents x and y:

$$\tilde{\tau} = \mathcal{L}^x \tau, \quad \tilde{H} = \mathcal{L}^y H. \tag{81.14}$$

Combining (81.13) and (81.14), we obtain

$$\Phi(\mathcal{L}^x \tau, \quad \mathcal{L}^y H) = \mathcal{L}^d \Phi(\tau, H). \tag{81.15}$$

Let us show now that from Eq. (81.15) it follows that all the critical exponents are expressed in terms of x and y, and make sure, in particular, that the Rushbrooke-Coopersmith and Griffith inequalities degenerate into equalities. Differentiating Eq. (81.15) with respect to H and using the fact that $(\partial\Phi/\partial H)_\tau = -M$, we find

$$\mathcal{L}^y M(\mathcal{L}^x \tau, \quad \mathcal{L}^y H) = \mathcal{L}^d M(\tau, H). \tag{81.16}$$

To find the critical parameter β, we assume $H = 0$. Formula (81.16) yields $M(\tau, 0) = \mathcal{L}^{y-d} M(\mathcal{L}^x \tau, 0)$. Since the parameter $\mathcal{L}$ is arbitrary within a wide range ($1 \ll \mathcal{L} < r_c/l$), we can take $\mathcal{L} = \tau^{-1/x}$; then we find

$$M(\tau, 0) = \tau^{(d-y)/x} M(1, 0)$$

and, consequently, in the relationship $M(\tau, 0) \propto \tau^\beta$ the exponent β is equal to

$$\beta = (d - y)/x. \tag{81.17}$$

Differentiating (81.16) with respect to H and assuming then $H = 0$, we find the expression for susceptibility $\chi_m = (\partial M/\partial H)_\tau|_{H=0}$:

$$\mathcal{L}^{2y} \chi_m(\mathcal{L}^x \tau, 0) = \mathcal{L}^d \chi_m(\tau, 0).$$

Choosing $\mathscr{L} = \tau^{-1/x}$ ($\tau > 0$), we obtain $\chi_m(\tau, 0) = \tau^{(d-2y)/x} \chi_m(1, 0)$, while assuming $\mathscr{L} = (-\tau)^{-1/x}$ ($\tau < 0$), the result is [see (76.6)]

$$\gamma' = \gamma = \frac{2y-d}{x}. \tag{81.18}$$

Assuming in (81.16) $\tau = 0$, we find

$$M(0, H) = \mathscr{L}^{y-d} M(0, \mathscr{L}^y H)$$

and, taking $\mathscr{L} = H^{-1/y}$, we obtain $M(0, H) = H^{(d-y)/y} M(0, 1)$, and, consequently, the exponent δ is equal to

$$\delta = \frac{y}{d-y}. \tag{81.19}$$

Since the exponents β, γ, γ' and δ are expressed in terms of two similarity parameters x and y, they must be interrelated. It can be readily verified that for any d the relating formula has the form

$$\gamma = \beta(\delta - 1). \tag{81.20}$$

This relationship is called the *Widom equation.*

Using the formula

$$C_H = T(\partial S/\partial T)_H = -T(\partial^2 \Phi/\partial T^2)_H$$

and assuming $H = 0$, we obtain from (81.15) $\mathscr{L}^{2x} C_H(\mathscr{L}^x \tau, 0) = \mathscr{L}^d C_H(\tau, 0)$, whence, taking $\mathscr{L} = (\pm\tau^{-1/x})$, we find for the exponent α and α' the expression

$$\alpha = \alpha' = \frac{2x-d}{x}. \tag{81.21}$$

It is readily seen from (81.17), (81.18), (81.19), (81.21) that in the theory of similarity Rushbrooke-Coopersmith and Griffith inequalities degenerate into equalities irrespective of the lattice dimension d.

We have investigated the physical content of the similarity hypothesis and some of its corrolaries considering by way of example a magnetic system. However, the most important characteristic of the present-day development of this theory is its universality: the theory is applicable to a rather wide class of physical systems. In addition to fluid and magnetic systems, it is applicable to phase transitions in ferroelectric materials, ordering alloys, liquid helium and superconductors. The common feature of all these systems is the possible introduction of the *local order parameter* $\varphi(\mathbf{r})$. Such a parameter can be the difference in the densities of a liquid and a vapour, magnetization density and density of polarization in magnetic and ferroelectric materials, the local value of the parameter $N_{A\alpha} - N_\alpha$ in alloys, etc. This parameter can be regarded as some classical field, an *ordering field*, similar to the sound or electromagnetic field, with this field fluctuating at any space point.

Close to the critical point, when the correlation radius increases infinitely, the peculiarities in the behaviour of the intra-atomic forces in the region with dimension $\mathscr{L}$, small compared with r_c, become immaterial. On the other hand, the fact that the only essential, from the phenomenological viewpoint, parameter with the dimension of length r_c vanishes in the system becomes very important. So, for similarity transformations $\mathbf{r} \to \lambda \mathbf{r}$ with a similarity parameter λ the strongly fluctuating physical quantities $A_i(\mathbf{r})$ must also change in a similar manner with some similarity parameter Δ_i, $A_i(\mathbf{r}) \to \lambda^{\Delta_i} A_i(\mathbf{r})$. In particular, the order parameter of $\varphi(\mathbf{r})$ must transform obeying the same law. The parameters x and y introduced above are particular cases of the parameters Δ_i. The most important object of the theory under consideration is the general calculation of the parameters Δ_i from microscopic equations. This problem is, however, far from being solved, and there exist only individual approximate methods for the solution of the problem (see [32], [34]).

Problems

1. Prove within the framework of the similarity hypothesis for a magnetic system the equalities $\gamma(\delta + 1) = (2 - \alpha) \times (\delta - 1)$ and $(2 - \alpha - \gamma)\delta = 2 - \alpha + \gamma$.
2. The energy gap exponents Δ_n for a magnetic material are determined by the formula

$$(\partial^n \Phi / \partial H^n)_\tau \sim \tau^{-\Delta_n} (\partial^{n-1} \Phi / \partial H^{n-1})_\tau.$$

Show that in the theory based on the similarity hypothesis the energy gap exponents Δ_n are independent of n.

Answer. $\Delta_n = y/x$.

3. Introduce the exponent ζ specified by the relationship $S(M) \propto M^{\zeta+1}$ ($T = T_{cr}$, $M \to 0$). Find the exponent ζ within the framework of the similarity hypothesis and prove the equality

$$(2 - \alpha')\zeta + 1 = (1 - \alpha')\delta.$$

Answer. $\zeta = \frac{y-x}{d-y}$.

PART THREE

ELEMENTS OF KINETICS AND NON-EQUILIBRIUM THERMODYNAMICS

So far we have considered equilibrium states and processes proceeding in macroscopic systems. This part of the book is devoted to a considerably more complicated problem—the investigation of *non-equilibrium* states and processes. The solution of this problem also permits two basically different approaches: the phenomenological and the microscopic.

In the first case the problem consists in establishing the relations between macroscopic parameters without the use of atomic and molecular representations in the implicit form. In distinction to thermodynamics of equilibrium processes, however, the main part in *non-equilibrium thermodynamics* is played by the fluxes of different thermodynamic quantities—mass, energy, momentum, entropy, charge, etc., that are absent in equilibrium states. The establishment of relations between the fluxes of different quantities and between the coefficients pertinent in these ralationships is the main object of non-equilibrium thermodynamics.

Along with this there also exists the second method of studying non-equilibrium processes, involving a further development and generalization of the methods of statistical physics. This method, the *kinetic* one, is based on atomic and molecular representations and it makes use of the description of a state with the aid of distribution functions introduced in statistical physics. In a non-equilibrium state the distribution functions by no means coincide with the equilibrium distribution functions defined in statistical physics, and in the general case of non-equilibrium states they depend on time. In addition, the non-equilibrium distribution functions depend on coordinates even in the absence of applied fields, whereas in equili

brium states the distribution is uniform in space in the absence of applied fields.

The main objects of kinetics consists, firstly, in finding the equations specifying the change of the distribution function in space and in time, and, secondly, in relating the micro- and macroscopic quantities, namely, in relating the distribution functions with the fluxes of quantities.

The problem of finding the distribution function for non-equilibrium states is more complicated than that of finding the distribution function in an equilibrium state.

For equilibrium states there exists a universal solution of the problem, the Gibbs distribution, while in non-equilibrium states the individual features of any system and the variety of the external factors acting upon the system have so strong effect, that the attempts to derive a universal formula for the distribution function proved fruitless. Moreover, even the kinetic equation describing the change of the distribution function in time and space can be obtained only in some limit cases, by making some more or less serious assumptions.

The range of concrete problems in kinetics and non-equilibrium thermodynamics is rather wide. These problems include, firstly, the *relaxation* problems concerning the transition from a preset initial non-equilibrium state to equilibrium; secondly, problems concerning the behaviour of macroscopic systems in *rapidly varying fields*, the characteristic time of which is small compared with the relaxation times of system's parameters, so that there is no time for the thermodynamic equilibrium to set in; thirdly, non-equilibrium, but *steady-state* processes in the course of which the gradients of system's parameters are maintained constant artificially by transferring heat, substance, charge, etc., to the boundaries of the sample. Processes of this kind include, for instance, *transport* phenomena—diffusion, heat conduction, viscosity, electric conductivity.

Until recently kinetics and non-equilibrium thermodynamics were used to investigate mainly weakly non-equilibrium states. In the last few years, however, rapid development has been found in the thermodynamics of living organisms—heavily non-equilibrium states in open systems, exchanging substance and energy with the surroundings, which is of paramount importance for biophysics.

The kinetic approach to the study of non-equilibrium phenomena is more profound and it must substantiate the formal methods of non-equilibrium thermodynamics. In the following sections, 82 through 96, we shall consider the main methods of classical kinetics, a brief description of some methods of quantum kinetics will be given in Sec. 97, and the fundamentals of phenomenological non-equilibrium thermodynamics will be outlined in Chap X

CHAPTER IX

KINETICS

82. The Smoluchowski Equation. The Principle of Detailed Balancing

Let us consider a monoatomic gas in a non-equilibrium state, returning to the concept of the μ-space (see Sec. 33), whose coordinates are three projections of the radius-vector **r** and three projections of the vector of momentum **p**, the state of the gas is characterized on the whole by the set of N representative points in a six-dimensional μ-space, moving along their phase trajectories.

Let us introduce the representative point density, or the distribution function $f(\mathbf{r}, \mathbf{p}, t)$, that in the general case of a non-equilibrium system depends both on coordinates and momenta, **r** and **p** and on the time t.

The space density of particles $n = n(\mathbf{r}, t)$ is related with the distribution function f by the expression

$$n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{p}, t)\, d^3p. \tag{82.1}$$

The particle density in the momentum space $n(\mathbf{p}, t)$ is analogously expressed by

$$n(\mathbf{p}, t) = \int f(\mathbf{r}, \mathbf{p}, t)\, d^3r. \tag{82.2}$$

The distribution function $f(\mathbf{r}, \mathbf{p}, t)$ is normalized by the condition

$$\int\int f(\mathbf{r}, \mathbf{p}, t)\, d^3r\, d^3p = N, \tag{82.3}$$

where N is the total number of gas particles.

One of the most important objects of physical kinetics consists in finding the distribution function $f(\mathbf{r}, \mathbf{p}, t)$. The knowledge of the distribution function makes it possible to solve a wide class of problems associated with non-equilibrium states of a system. These problems include the calculation of *kinetic coefficients* for transport phenomena, such as heat conduction, diffusion, etc.

Let, for instance, ψ be some additive physical quantity, e.g. the molecular kinetic energy reduced to one molecule, the momentum of the molecule. Then, the expressions

$$\overline{\psi} = \frac{\int f\psi\, d^3p}{\int f\, d^3p}, \quad \overline{\psi u_i} = \frac{\int f\,(p_i/m)\,\psi\, d^3p}{\int f\, d^3p} \tag{82.4}$$

represent the space density and the flux density for the macroscopic quantity ψ.

In classical kinetics the investigation method for non-equilibrium processes essentially depends on whether the gas under consideration is "dense" or rarefied. Let us set a criterion permitting a more exact identification of these notions.

In Secs. 82 through 88 we shall limit ourselves to the consideration of gases consisting of neutral particles. For such gases the molecular interaction forces decrease rapidly with increasing intermolecular spacing, and there exists a sufficiently definite range of molecular interaction, denoted by r_0. The quantity r_0 depends on temperature, but for not very high temperatures this dependence is rather weak and r_0 can be assumed to be constant of the order 10^{-7} to 10^{-8} cm. In fact, r_0 must be defined as the distance between molecules at which the potential energy of molecular interaction becomes of the same order of magnitude as their mean kinetic energy $\sim T$. The direction-averaged potential energy of the intramolecular attractive forces is inversely proportional to r^6, therefore, $r_0 \propto T^{-1/6}$. Until the distance between two molecules is greater than r_0, molecular motion is due only to the action of an applied field (if such is present) and only at intermolecular distances smaller than r_0 the molecular interaction changes essentially the nature of their motion.

Let us assume the gas to be so rarefied that the mean free path l of a molecule is much larger than the range af action of intermolecular forces and, correspondingly, the mean free time τ is much greater than the molecular interaction time τ_0. Since the order of magnitude of the free path is $1/nr_0^2$, where n is the molecular density, the validity criterion for this approximation has the form $1/nr_0^2 \gg r_0$ or $n \ll r_0^{-3}$.

In accordance with the estimate assumed, $r_0 \sim 10^{-7}$ to 10^{-8} cm, whence $n \ll (10^{21}$ to $10^{24})$ cm^{-3}. We can, then, introduce the concept of molecular "collision" by which is meant the change in the motion of each molecule occurring during the time one of the molecules spends within the sphere of action of the other molecule. By virtue of the inequality $\tau \gg \tau_0$, the process of collision can be assumed to be instantaneous. Since molecular velocities are finite, the change in molecular coordinates during the collision time, $\Delta x_i = v_i\tau_0$, can be taken as zero, but the change in the velocity projection or in the molecular momentum $\Delta v_i = w_0\tau_0$ and $\Delta p_i = F_i\tau_0$ has a finite value. We must assume that as $\tau_0 \to 0$ the acceleration w_i and the intermolecular force F_i increase infinitely, so that the products $w_i\tau_0$ and $F_i\tau_0$ tend to a finite limit.

Thus, in this approximation [Fig. 108 (*a*)] molecular collision is accompanied only by a discontinuity jump in the momentum of the two molecules. At the moment of collision the phase point representing a molecule in the μ-space passes abruptly from one position into the other, due to the jumpwise change in momentum, and by virtue of this the continuity equation for the distribution function in the

μ-space becomes invalid in the assumed approximation. This means that in the μ-space there exist sources and sinks of the distribution function, the intensity of which is determined by the molecular collisions. The approximation described above will be examined in greater detail in Secs. 85 through 87.

In the opposite limiting case of dense gases ($nr_0^3 \gg 1$) [Fig. 108 (*b*)] $\lambda \ll r_0$, $\tau \ll \tau_0$. In this case, evidently, the concept of collision loses its meaning at all, since a molecule constantly finds itself in the range of action of neighbouring molecules. This limiting case will be considered below.

Since each particle interacts simultaneously with a very large number of adjacent particles, its effect on the distribution of the other particles is insignificant. For this reason the determination of the distribution functions for a system of particles is reduced to the problem concerning the motion of a single particle in the field created by

FIG. 108

other particles. Due to the motion of the particles this field fluctuates, and the motion of a selected particle is a *stochastic* random process. For such random processes we can introduce the concept of probability of the particle's passing from point x into the elementary volume dy around point y in time τ. The symbols x and y are used to denote points, the symbol dy—elementary volume in the μ-space. Denoting by $W(y, x \mid \tau, t)$ the probability density of the transition from point x to point y in time τ, we obtain for the probability of transition

$$dw = W(y, x \mid \tau, t)\, dy, \tag{82.5}$$

where t is the time when the representative point leaves x.

It should be noted that formula (82.5) already describes some hypothesis on the course of the process. The fact is that in the general case the probability of transition from x to y can depend not only on the arguments indicated in (82.5), but also on the prehistory of the particle—coordinates and momenta in moments of time preceding t. If only two successive events are correlated, such processes are referred to as *Markov chains*. In other words, in Markov processes the possibility of transition from one point to the other is independent of the prehistory of the process, i.e. the particle has no

"memory". The Markov model describes with a good degree of accuracy the kinetic processes in very dense gases.

Let us consider a successive transition of a particle from x to y through point z in time $t + \tau$, where t is the time of transition from x to z, and τ — from z to y.

Since the processes of transition from x to z and from z to y are independent, the probability of transition from x into the interval dy through an intermediate point accurate to dz can be expressed by

$$W(y, z \mid \tau, t_0 + t)\, W(z, x \mid t, t_0)\, dz\, dy.$$

To find $W(y, x \mid t + \tau, t_0)$, it is sufficient to integrate this product over all positions of the intermediate point z. As is seen from Fig. 109, at any choice of the intermediate time $t_0 + t$ we examine all phase trajectories originating at point x at the moment of time t_0 and running to y at the moment of time $t_0 + t + \tau$. We obtain for the function W the non-linear integral equation

$$W(y, x \mid t + \tau, t_0) = \int dz\, W(y, z \mid \tau, t_0 + t)\, W(z, x \mid t, t_0), \qquad (82.6)$$

called the *Smoluchowski equation*.

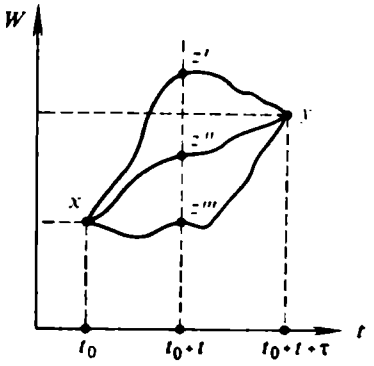


FIG. 109

It should be emphasized that in deriving this equation we only used the definition of the probability of transition for a Markov process and the probability multiplication and summation theorems. In this connection the Smoluchowski equation is of a rather general nature and its field of application is very wide.

Let us introduce now an important physical law, called the *principle of detailed balancing*. The laws determining the change in the microstates of a system in time are either the laws of classical mechanics or the laws of quantum mechanics. For a closed system the former and the latter laws are symmetrical with respect to the change of the sign of time, i.e. to the replacement of t by $-t$.

In classical mechanics the above statement follows from the fact that the basic equation of classical mechanics,

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i,$$

is of the second order with respect to time. For this reason when replacing t by $-t$ the left-hand side of this equation is invariant, and the right-hand side does not contain t explicitly at all.

In the quantum mechanics of spinless particles this follows from the fact that the replacement of t by $-t$ converts Schrödinger's equation for the wave function $\psi(q_i, t)$ of a system,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{\mathcal{H}}\psi,$$

into the equation for a complex conjugate function:

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \hat{\mathcal{H}}\psi^*$$

(for a system of spinless particles the Hamiltonian $\hat{\mathcal{H}}$ is real). The complex conjugate wave function $\psi^*(q_i, t)$ describes the same state as $\psi(q_i, t)$, but with a changed sign of the vector of the probability density flux $\mathbf{j}$. On the other hand, when time t is replaced by $-t$, the initial and final states of the system change places. Therefore, the probabilities of a direct and reverse transitions $x \to y$ and $y \to x$ must be the same, and the function $W(y, x \mid \tau, t)$ must be symmetric with respect to the first pair of arguments:

$$W(y, x \mid \tau, t) = W(x, y \mid \tau, t). \tag{82.7}$$

This assertion is called the *principle of detailed balancing*.

This principle is derived in this form for a closed system of spinless particles; it also remains valid in the case when the system is in a time-independent applied field—all the preceding reasoning also hold in this case. In the case of a system with particles having spin moments, relationship (82.7) does not hold. The principle of detailed balancing can, however, be shown to be true for all spin averaged initial and final state probabilities (see, for example [35], [36]).

It should be noted finally that the name "principle of detailed balancing" is associated with the fact that equation (82.7) holds for any pair of points x, y and that the dynamic equilibrium of the occupation numbers is maintained by the direct $x \rightleftarrows y$ transitions and not by the transitions of the $x \to y$ kind by means of intermediate states z.

83. The Fokker-Planck Equation. Brownian Motion

The Smoluchowski integral equation (82.6) derived in the preceding section can be transformed into a linear differential equation following the method due to Pontryagin.

We write down Eq. (82.6) in the form

$$W(y, x \mid t + \tau, 0) = \int dz\, W(y, z \mid \tau, t)\, W(z, x \mid t, 0), \tag{83.1}$$

assuming $t_0 = 0$.

Let us introduce the function $g(x)$, integrable in the μ-space and satisfying the boundary conditions: the function $g(x)$ and all its derivatives of any order vanish as $|x| \to \infty$:

$$g(x) \to 0, \quad \frac{\partial g}{\partial x_i} \to 0, \quad \frac{\partial^2 g}{\partial x_i \partial x_k} \to 0, \ldots . \tag{83.2}$$

We multiply Eq. (83.1) by $g(y)\,dy$ and integrate it over all values of y:

$$\int W(y, x|t+\tau, 0)\, g(y)\, dy$$

$$= \int\int W(y, z|\tau, t)\, W(z, x|t, 0)\, g(y)\, dy\, dz. \tag{83.3}$$

We expand $g(y)$ on the right-hand side of the equation into a Taylor series in $(y_i - z_i)$:

$$g(y) = g(z) + \frac{\partial g}{\partial z_i}(y_i - z_i) + \frac{1}{2}\frac{\partial^2 g}{\partial z_i \partial z_k}(y_i - z_i)(y_k - z_k) + \ldots$$

(by repeating indices is meant summation from 1 to 6). Substituting this expansion into the right-hand side of Eq. (83.3), we obtain

$$\int W(y, x|t+\tau, 0)\, g(y)\, dy$$

$$\int\int \left[g(z) + \frac{\partial g}{\partial z_i}(y_i - z_i) + \frac{1}{2}\frac{\partial^2 g}{\partial z_i \partial z_k}(y_i - z_i)(y_k - z_k) + \ldots \right]$$

$$\times W(y, z|\tau, t)\, W(z, x|t, 0)\, dy\, dz. \tag{83.4}$$

Integrating the first term on the right-hand side of Eq. (83.4) over y and accounting for the normalization condition $\int W(y, x|\tau, t)\, dy = 1$, we can rewrite Eq. (83.4) to read

$$\int g(y)\, \frac{W(y, x|t+\tau, 0) - W(y, x|t, 0)}{\tau}\, dy$$

$$- \int a_i^{(\tau)}(z, t)\, \frac{\partial g}{\partial z_i}\, W(z, x|t, 0)\, dz$$

$$- \frac{1}{2}\int b_{ik}^{(\tau)}(z, t)\, \frac{\partial^2 g}{\partial z_i \partial z_k}\, W(z, x|t, 0)\, dz - \ldots = 0, \tag{83.5}$$

where the following notations are introduced:

$$a_i^{(\tau)}(z, t) = \frac{1}{\tau}\int (y_i - z_i)\, W(y, z|\tau, t)\, dy,$$

$$b_{ik}^{(\tau)}(z, t) = \frac{1}{\tau}\int (y_i - z_i)(y_k - z_k)\, W(y, z|\tau, t)\, dy,$$

. . . . . .

The six-dimensional vector $a_i^{(\tau)}(z, t)$ is the mean velocity of a representative point in the μ-space during time τ at point z and at the

instant of time t. The six-dimensional tensor $b_{ik}^{(\tau)}(z, t)$ is the function of the correlation between the ith and kth projections of the displacement of a representative point during time τ, reduced to unit time, and the spur of this tensor gives the mean square of the displacement of the representative point during time τ reduced to unit time:

$$b_{ii}^{(\tau)} = \frac{1}{\tau} \int (y_i - z_i)^2 W(y, z|\tau, t)\, dy.$$

It is clear that the higher-order expansion coefficients in (83.5) represent the correlations and the mean degrees of displacement of the representative point of a higher order. It will be assumed below that for small values of τ the higher-order terms of the expansion are small compared with the first two, and they will be ignored, since for small τ the probability of large displacements $(y_i - z_i)$ is small and the higher the power n of the difference $(y_i - z_i)$ in the integrand, the smaller the corresponding correlation coefficient.

Let us pass now in Eq. (83.5) to the limit as $\tau \to 0$ and denote

$$a_i(z, t) = \lim_{\tau \to 0} a_i^{(\tau)}(z, t), \quad b_{ik}(z, t) = \lim_{\tau \to 0} b_{ik}^{(\tau)}(z, t).$$

The second and third terms will, then, be transformed as follows

$$\int a_i(z, t)\, W(z, x|t, 0) \frac{\partial g}{\partial z_i}\, dz = \int \left\{ \frac{\partial}{\partial z_i} [a_i(z, t)\, W(z, x|t, 0)\, g(z)] - g(z) \frac{\partial}{\partial z_i} [W(z, x|t, 0)\, a_i(z, t)] \right\} dz, \quad (83.6)$$

$$\frac{1}{2} \int b_{ik}(z, t)\, W(z, x|t, 0) \frac{\partial^2 g}{\partial z_i\, \partial z_k}\, dz = \frac{1}{2} \int \left\{ \frac{\partial}{\partial z_i} \left[b_{ik}(z, t)\, W(z, x|t, 0) \frac{\partial g}{\partial z_k} \right] - \frac{\partial}{\partial z_k} \left[g(z) \frac{\partial}{\partial z_i} b_{ik}(z, t)\, W(z, x|t, 0) \right] + g(z) \frac{\partial^2}{\partial z_i\, \partial z_k} [b_{ik}(z, t)\, W(z, x|t, 0)] \right\} dz. \quad (83.7)$$

The first term on the right-hand side of Eq. (83.6) and the first two terms in (83.7) can be transformed by means of the Gauss theorem into an integral over an infinitely remote boundary surface, and they will vanish, due to the boundary conditions (83.2). Denoting in the remaining terms the integration variable by y, we obtain from Eq. (83.5)

$$\int g(y) \left\{ \frac{\partial W(y, x|t, 0)}{\partial t} + \frac{\partial}{\partial y_i} [W(y, x|t, 0)\, a_i(y, t)] - \frac{1}{2} \frac{\partial^2}{\partial y_i\, \partial y_k} [W(y, x|t, 0)\, b_{ik}(y, t)] \right\} dy$$

whence, due to the arbitrariness of function $g(y)$, at any finite y we have the equation

$$\frac{\partial W(y, x|t, 0)}{\partial t} + \frac{\partial}{\partial y_i}[W(y, x|t, 0)\, a_i(y, t)] - \frac{1}{2}\frac{\partial^2}{\partial y_i \partial y_k}[W(y, x|t, 0)\, b_{ik}(y, t)] = 0. \quad (83.8)$$

Equation (83.8) is called the *Fokker-Planck* or the monomolecular kinetic *equation*. This name reflects the fact that the problem on the collective motion of system's particles was reduced to the problem about wandering of one particle with an averaging over the arrangement of the remaining particles.

Let us find the relation between the transition probability density $W(y, x \mid \tau, t)$, and the distribution function $f(\mathbf{r}, \mathbf{p}, t) = f(x, t)$. Let at $t = 0$ the distribution function at point x in the μ-space be equal to $f(x, 0)$. The change in the number of particles in volume dx in time t, i.e. the difference between the number of particles leaving the volume dx and the number of particles entering volume dx in the same time, is expressed by

$$[f(x, t) - f(x, 0)]\, dx = dx \int [W(x, z|t, 0)\, f(z, 0) - W(z, x|t, 0)\, f(x, 0)]\, dz.$$

Cancelling out dx and allowing for the normalization condition $W(z, x \mid t, 0) = 1$, we obtain the equation

$$f(x, t) = \int W(x, z \mid t, 0)\, f(z, 0)\, dz, \quad (83.9)$$

showing that the multiplication by $W(x, z \mid t, 0)$ and integration over z is equivalent to a simultaneous displacement in the μ-space through vector $(x - z)$ and in time through segment t.

Multiplying Eq. (83.8) by $f(x, 0)$ and integrating over x, we obtain the Fokker-Planck equation for the distribution function $f(y, t)$:

$$\frac{\partial f(y, t)}{\partial t} + \frac{\partial}{\partial y_i}[f(y, t)\, a_i(y, t)] - \frac{1}{2}\frac{\partial^2}{\partial y_i \partial y_k}[f(y, t)\, b_{ik}(y, t)] = 0.$$

The above equation can be presented in the form of the continuity equation in the μ-space:

$$\frac{\partial f}{\partial t} + \frac{\partial j_k}{\partial y_k} = 0,$$

where the components of the six-dimensional flux density vector are

$$j_k = a_k(y, t)\, f(y, t) - \frac{1}{2}\frac{\partial}{\partial y_i}[b_{ik}(y, t)\, f(y, t)]. \quad (83.10)$$

This mathematical statement of the Fokker-Planck equation paves the way to some generalizations. The symbols x, y, ... will

be used to denote points not in the μ-space but in a three-dimensional space. The reasonings leading us to the Fokker-Planck equation are also valid in this case, and we shall obtain Eq. (83.9) with a flux density expressed by (83.10), but in a three-dimensional space. Vector a_k represents, then, the ordinary particle's velocity **v**, and tensor b_{ik} the function of the correlation between the displacements of the particle in the directions of the coordinate axes.

Let us consider a gas in the absence of an applied field. In this case, due to the homogeneity of time and space the transition probability density can depend only on the distance between the points and is independent of time:

$$W(y, x \mid \tau, t) = W(\mid y - x \mid, \tau).$$

Therefore for $a_i(y, t)$, $b_{ik}(y, t)$ we have

$$a_i(y, t) = \lim_{\tau \to 0} \frac{1}{\tau} \int W(|y-x|, \tau)(y_i - x_i)\, dx$$

$$= \lim_{\tau \to 0} \frac{1}{\tau} \int W(|z|, \tau)\, z_i\, dz$$

by virtue of the fact that the integrand is odd and

$$b_{ik}(y, t) = \lim_{\tau \to 0} \frac{1}{\tau} \int W(|y-x|, \tau)(y_i - x_i)(y_k - x_k)\, dx = b\delta_{ik},$$

where

$$b = \lim_{\tau \to 0} \frac{1}{\tau} \int W(|z|, \tau)\, z_k^2\, dz = \text{const}.$$

The Fokker-Planck equation then acquires the form

$$\frac{\partial f}{\partial t} = \frac{1}{2} b \nabla^2 f$$

and accurate to the notation it coincides with the diffusion equation

$$\frac{\partial f}{\partial t} = D \nabla^2 f.$$

From this we have the Einstein relation for the coefficient b and the diffusion coefficient D:

$$b = 2D.$$

By the symbol x will now be meant the coordinate not of a molecule but of a Brownian particle suspended in a gas or liquid. It is readily seen that the Fokker-Planck equation describes approximately the wandering of a particle in this case as well. Then, for the formula for the coefficient $b_{ii}^{(\tau)}$, which is valid for the three-

mensional case, we obtain the expression,

$$\overline{\Delta x^2} = 3b\tau = 6D\tau,$$

according to which the mean square displacement of the Brownian particle is proportional to time.

When Brownian particles are placed in an applied field, the first term in the expression for flux, (83.10), also differs from zero. Ignoring the dependence of the coefficient b on the coordinates, which is rigorously valid for homogeneous fields and approximately true for inhomogeneous fields on small segments, we obtain for the flux $\mathbf{j}$ the expression

$$\mathbf{j} = \mathbf{a}f - \frac{1}{2} b\nabla f.$$

In an equilibrium state particle's distribution is described by Boltzmann's formula

$$f = f_0 e^{-\mathcal{U}(x, y, z)/T},$$

and the flux $\mathbf{j}$ is equal to zero, and, consequently, we have

$$f_0 \left(\mathbf{a} + \frac{1}{2} \frac{b\nabla \mathcal{U}(x, y, z)}{T}\right) e^{-\mathcal{U}(x, y, z)/T} = f_0 \left(\mathbf{a} - \frac{b\mathbf{F}}{2T}\right) e^{-\mathcal{U}(x, y, z)/T} = 0,$$

$$\mathbf{a} = \frac{b\mathbf{F}}{2T} = \frac{D\mathbf{F}}{T} = q\mathbf{F},$$

where $q = D/T$ is *mobility*,
$\mathbf{F} = -\nabla \mathcal{U}$ is force.

We have received the Stokes law for the resistance offered by a viscous liquid to the motion of a particle, according to which this resistance is proportional to velocity to the first power. For spherical particles [37] we have

$$q = 1/6\pi\eta r$$

where η = dynamic viscosity,
r = radius of the particle.

The formula for the mean square of displacement reduces to

$$\overline{\Delta x^2} = kT/\pi\eta r.$$

This formula was used at one time to measure the constant k and the Avogadro number $N_A = R/k$, and it confirmed the existence of atoms.

Problem

Derive the Fokker-Planck equation for a three-dimensional density of Brownian particles $f(\mathbf{r}, t)$, assuming that the Brownian particles are acted upon by a friction force proportional to velocity, $-\gamma\mathbf{v}$, and that the density of the friction force and external force is balanced at each point by the pressure gradient $-f(\gamma\mathbf{v} + \nabla\mathcal{U}) = \nabla P = \nabla(fT)$.

Answer. $\frac{\partial f}{\partial t} + \frac{1}{\gamma}\nabla(f\mathbf{F}) - \frac{1}{\gamma}\nabla^2(fT) = 0.$

84. Kinetic Balance Equation. Einstein's Derivation of Planck's Formula

Let us return to the equation relating the function $f(x, t)$ with the transition probability density $W(y, x \mid \tau, t)$.

We expand the transition probability density $W(y, x \mid \tau, t)$ for small τ into a power series in τ. Limiting ourselves to the first terms of the expansion, we obtain

$$W(y, x \mid \tau, t) = \Phi(y, x, t) + \tau P(y, x, t), \tag{84.1}$$

where $P(y, x, t)$ is the probability of transition from point x to point y at the instant of time t per unit time, and $\Phi(y, x, t)$ represents the probability of "instantaneous" transition from x to y.

Since in a zero time interval the particle cannot leave point x, the zero-power term in τ can be presented in the form

$$\Phi(y, x, t) = A(y, t)\,\delta(y - x). \tag{84.2}$$

From the normalization condition

$$\int W(y, x \mid \tau, t)\,dy = 1 \tag{84.3}$$

we find, using Eq. (84.1), that

$$A(x, t) = 1 - \tau\int P(y, x, t)\,dy. \tag{84.4}$$

Using Eq. (84.4), we find the expression for the transition probability density

$$W(y, x \mid \tau, t) = \left\{1 - \tau\int P(z, y, t)\,dz\right\}\delta(y - x) + \tau P(y, x, t). \tag{84.5}$$

Let us rewrite the previously derived relation (83.9) to read

$$f(y, t + \tau) = \int W(y, x \mid \tau, t)\,f(x, t)\,dx.$$

Substituting Eq. (84.5) into the above expression and passing to the limit $\tau \to 0$, we obtain upon simple computations the following equation:

$$\frac{\partial f(x, t)}{\partial t} = \int [P(x, z, t) f(z, t) - P(z, x, t) f(x, t)] dz \qquad (84.6)$$

The left-hand side of Eq. (84.6) represents the change in the particle density at point x at the instant of time t per unit time. This change is due to the arrival of particles to point x from all other points z (the first term on the right-hand side) and the departure of particles from point x (the second term). For this reason Eq. (84.6) is referred to as the *kinetic balance equation.*

In this equation we can pass from the classical description of states in the μ-space to the quantum-mechanical discrete states. We must, then, replace the distribution function $f(x, t)$ by the number of particles in the ith state, $N_i(t)$, and the probability $P(x, z, t)$ of transition per unit time from point z to point x by the probabilities P_{ik} of transition from the kth to the ith state. Equation (84.6) acquires, then, the form

$$\frac{dN_i}{dt} = \sum_{k \neq i} (P_{ik} N_k - P_{ki} N_i). \qquad (84.7)$$

If the system is closed, then the principle of detailed balancing is valid, which for the probabilities of transition per unit time can be presented in the form

$$P(x, y, t) = P(y, x, t), \qquad (84.8)$$

or

$$P_{ik}(t) = P_{ki}(t). \qquad (84.9)$$

As has been already mentioned above, for particles with spin by $P(x, y, t)$ or $P_{ik}(t)$ are to be meant the probabilities averaged over the spins of the initial and final states.

It should be noted that in the general case the probabilities of transition $P(x, z, t)$ or $P_{ik}(t)$ are functions of the occupation numbers $f(x, t)$ or $N_i(t)$. Therefore Eqs. (84.6), (84.7) only seem to be simple; actually in the general case they are non-linear integro-differential equations, an approximate solution of which is possible only in the simplest cases with more or less serious assumptions.

Let us consider by way of a simple example an ideal gas consisting of atoms with two nondegenerate energy levels ε_1 and ε_2. We assume the gas to be in contact with a thermostat whose action on the gas induces the transitions of atoms from one state to another. Due to the fact that the transitions are provoked not by atomic collisions but by an external action, the transition probabilities P_{12} and P_{21} will be assumed independent of the occupation numbers and of

time. It should be noted that since the gas is an open system, the principle of detailed balancing is invalid, i.e. $P_{12} \neq P_{21}$.

The kinetic balance equations have the form

$$\frac{dN_1}{dt} = P_{12}N_2 - P_{21}N_1, \quad \frac{dN_2}{dt} = P_{21}N_1 - P_{12}N_2. \qquad (84.10)$$

We look for the solution of the system in the form $N_i = C_i e^{\alpha t}$; then

$$(\alpha + P_{21})C_1 - P_{12}C_2 = 0, \quad -P_{21}C_1 + (\alpha + P_{12})C_2 = 0. \qquad (84.11)$$

The condition of the existence of a non-trivial solution of this system is the equality to zero of the determinant

$$\alpha[\alpha + P_{12} + P_{21}] = 0,$$

whence we have two roots

$$\alpha_1 = 0, \quad \alpha_2 = -P_{12} - P_{21}. \qquad (84.12)$$

The first solution gives the equilibrium state

$$N_1^{(1)} = C_1, \quad N_2^{(1)} = C_2 = C_1 \frac{P_{21}}{P_{12}},$$

and by virtue of the condition $N_1 + N_2 = N$, we have

$$N_1^{(1)} = \frac{NP_{12}}{P_{12}+P_{21}}, \quad N_2^{(1)} = \frac{NP_{21}}{P_{12}+P_{21}}.$$

The second solution yields the exponentially decreasing deviations from the stationary state:

$$N_{1,2}^{(2)} = \pm ne^{-(P_{12}+P_{21})t},$$

and, consequently, the general solution describes a relaxation process of approach to steady-state conditions:

$$N_1 = \frac{NP_{12}}{P_{12}+P_{21}} + ne^{-t/\tau}, \quad N_2 = \frac{NP_{21}}{P_{12}+P_{21}} - ne^{-t/\tau}, \qquad (84.13)$$

where n is determined by the initial conditions ($n = N_1 - N_1^{(1)} = N_2^{(1)} - N_2$ at $t=0$), and the relaxation time $\tau = \frac{1}{(P_{12}+P_{21})}$. It should be noted that $P_{12}/P_{21} = N_1^{(1)}/N_2^{(1)}$.

If the gas is not degenerate, then, using the Maxwell-Boltzmann distribution, we find

$$\frac{P_{12}}{P_{21}} = e^{(\varepsilon_2 - \varepsilon_1)/T}.$$

If $\varepsilon_1 < \varepsilon_2$ and $(\varepsilon_2 - \varepsilon_1)/T \gg 1$, then $P_{21} \ll P_{12}$ and $\tau \approx 1/P_{12}$.

Let us consider now a more complicated case of a system of atoms in equilibrium with electromagnetic radiation. This problem was

treated by A. Einstein in 1916, and he produced a kinetic proof of Planck's formula for the energy of luminous radiation.

Let us consider atoms in states with energies ε_i and ε_k (we do not limit ourselves any longer to the case of a two-level system) and, in accordance with the principle of detailed balancing, equate the number of transitions per unit time $i \to k$ and $k \to i$. We shall assume $\varepsilon_i > \varepsilon_k$, so that the transitions $i \to k$ occur with radiation of energy $\varepsilon_i - \varepsilon_k$, and the transitions $k \to i$ with the absorption of the same amount of energy.

The number of transitions with energy absorption is proportional to $\rho(\nu, T)$, which is the density of radiant energy with frequency ν corresponding to the transition $i \rightleftarrows k$ and to the number of atoms in the kth state, N_k. Denoting the proportionality factor by B_{ki}, we obtain for the number of $k \to i$ transitions, n_{ki}, the expression

$$n_{ki} = B_{ki} N_k \rho(\nu, T). \tag{84.14}$$

The reverse transitions $i \to k$, i.e. the transitions with radiation, can occur spontaneously (spontaneous radiation) The number of such transitions is proportional to the number of atoms with energy ε_i:

$$n_{ik}^{\text{sp}} = A_{ik} N_i, \tag{84.15}$$

where A_{ik} is the coefficient of spontaneous radiation.

The hypothesis introduced by Einstein consists in that, in addition to processes of spontaneous radiation, there exist radiation processes induced by the already existing radiation with frequency ν. For these induced transitions the radiation with frequency ν plays the part of a trigger mechanism, and such processes do not exist when the density of radiation with frequency ν is equal to zero. It is clear that the number of induced transitions n_{ik}^{ind} is proportional to the density of radiation $\rho(\nu)$ and to the number of atoms with energy ε_i.

$$n_{ik}^{\text{ind}} = B_{ik} \rho(\nu) N_i, \tag{84.16}$$

where B_{ik} is the coefficient of induced radiation. In a steady state we have

$$n_{ki} = n_{ik}^{\text{sp}} + n_{ik}^{\text{ind}}, \tag{84.17}$$

or

$$B_{ki} N_k \rho(\nu, T) = A_{ik} N_i + B_{ik} N_i \rho(\nu, T). \tag{84.18}$$

In equilibrium the numbers N_i and N_k must satisfy the Maxwell-Boltzmann distribution, since the gas of atoms is nondegenerate at any temperatures practically attainable (see Sec. 37):

$$\frac{N_k}{N_i} = \frac{g_k}{g_i} e^{(\varepsilon_i - \varepsilon_k)/T}. \tag{84.19}$$

From Eq. (84.19) we find

$$\rho(\nu, T) = \frac{A_{ik}}{B_{ki}\frac{N_k}{N_i} - B_{ik}} = \frac{A_{ik}g_i/B_{ki}g_k}{e^{(\varepsilon_i-\varepsilon_k)/T} - \frac{B_{ik}g_i}{B_{ki}g_k}}. \qquad (84.20)$$

For expression (84.20) to increase infinitely as $T \to \infty$, we must assume that the principle of detailed balancing, $B_{ik}g_i = B_{ki}g_k$, is valid for the induced radiation and absorption with frequency ν. Then we have

$$\rho(\nu, T) = \frac{A_{ik}/B_{ik}}{e^{(\varepsilon_i-\varepsilon_k)/T} - 1}.$$

According to the Wien thermodynamic law (Sec. 17), the function $\rho(\nu, T)$ must have the form $\nu^3 f(\nu/T)$, by virtue of which we must assume that

$$\varepsilon_i - \varepsilon_k = h\nu, \quad A_{ik}/B_{ik} = A\nu^3;$$

then

$$\rho(\nu, T) = \frac{A\nu^3}{e^{h\nu/T} - 1}. \qquad (84.21)$$

The constant A in (84.21) can be found, for instance, by the limit transition $h\nu/T \ll 1$ and comparing the result with the Rayleigh–Jeans equation (Sec. 17), $\rho(\nu, T) = \frac{8\pi T}{c^3}\nu^2$. Now we find $A = 8\pi h/c^3$, and formula (84.21) becomes identical with Planck's radiation formula given in Sec. 17.

The reader's attention should be drawn to the essential role played by induced radiation in the theory of quantum radiation amplifiers and oscillators. Let us assume that a monochromatic or almost monochromatic beam of light with frequency $\nu = (\varepsilon_i - \varepsilon_k)/h$ gets into a medium containing atoms with energy levels ε_i. This radiation will be partly absorbed by the atoms occupying the level ε_k, with the absorbed energy I_a being proportional to the number of transitions $k \to i$ and energy $h\nu = \varepsilon_i - \varepsilon_k$. According to formula (84.14), we have

$$I_a = n_{ki}h\nu = B_{ki}N_k\rho(\nu, T)\,h\nu.$$

On the other hand, atoms in the state with energy ε_i emit waves with frequency ν both spontaneously and on compulsion.

Spontaneous radiation differs from incident, however, in the direction of propagation and polarization. For this reason when composing the energy balance for coherent and incident waves, only induced radiation should be taken into account. According to Eq. (84.16), induced radiant energy is equal to

$$I_e = B_{ik}\rho(\nu, T)\,N_i h\nu.$$

The difference between the emitted and absorbed energy is

$$I = I_e - I_a = \rho(\nu, T)(B_{ik}N_i - B_{ki}N_k)h\nu.$$

It is seen from the above formula that the surroundings can serve as a radiation amplifier, or possess negative absorption, if $B_{ik}N_i - B_{ki}N_k > 0$, i.e. if the population inversion is created

$$\frac{N_i}{N_k} > \frac{B_{ki}}{B_{ik}} = \frac{g_i}{g_k},$$

i.e. the number of atoms with energy ε_i, calculated for one state $n_i = N_i/g_i$, is greater than the same number $n_k = N_k/g_k$ for the lower level ε_k.

As was shown in Sec. 67, such inversion can formally be described as a state with negative temperature $T < 0$. This state must be created and maintained by means of a continuous or pulsed "pumping" of particles to the upper level. The methods of effecting such pumping will not be treated here. The described effect forms the foundation of quantum amplifiers and oscillators of electromagnetic waves, lasers and masers.

Problem

Solve the kinetic balance equation (84.7) for a radioactive family of n elements, assuming that only the probabilities $P_{i,i+1} = \lambda_i$ ($\lambda_n = 0$, $\lambda_i > 0$) differ from zero. The initial conditions are $N_1 = N$, $N_i = 0$ ($i > 1$) at $t = 0$.

85. The Boltzmann Kinetic Equation

Let us turn to the study of rarefied gases, assuming in this section particle's coordinates x_1, x_2, x_3 and velocity projections v_1, v_2, v_3 to be the arguments of the distribution function and not momentum coordinates and projections. The kinetic equation to be derived here acquires, then, a more convenient form. The coordinates of the μ space will respectively be the quantities x_i, v_i ($i = 1, 2, 3$). The representative points are distributed over the μ-space with a density

$$f(\mathbf{r}, \mathbf{v}, t) = f(x_1, x_2, x_3, v_1, v_2, v_3).$$

The motion of the representative points along the phase trajectories can be regarded formally as the flow of some fluid. If no collisions between particles existed, the change in the density of representative points would be described by the continuity equation for a six-dimensional space:

$$\frac{\partial f}{\partial t} + \nabla_k j_k = 0. \qquad (85.1)$$

The components of the current density vector in the μ-space are equal to fv_i and fw_i $(i = 1, 2, 3)$, where $w_i = dv_i/dt$ are the projections of particle's acceleration. The more detailed form of Eq. (85.1) is

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial x_k}(fv_k) + \frac{\partial}{\partial v_k}(fw_k) = 0. \tag{85.2}$$

In the second and third terms the factors v_k and w_k can be taken out of the derivative sign, since according to the Hamilton equations

$$mw_k = -\frac{\partial \mathcal{H}}{\partial x_k}, \qquad mv_k = \frac{\partial \mathcal{H}}{\partial v_k}$$

we have

$$\frac{\partial v_k}{\partial x_k} + \frac{\partial w_k}{\partial v_k} = 0.$$

The projections w_k differ from zero only if the gas is placed in an applied field.

As has been already stated in Sec. 82, intermolecular collisions lead to a jumpwise change in the velocity projections at constant coordinates and, consequently, to a jumpwise displacement of the representative points in the μ-space. In this approximation the representative points "vanish" in some parts of the μ-space and are "born" in other parts without intersecting the boundaries of the volume separated in the μ-space. This means that the "instantaneous" collision approximation makes us to introduce on the right-hand side of the continuity equation sources and sinks for molecules with a given velocity at the given space point. Equation (85.2), therefore, is replaced by the equation

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} = J = q_{\text{sour}} - q_{\text{sink}}, \tag{85.3}$$

where J is called the *collision integral*, and the quantities q_{sour} and q_{sink} represent the strength of the sources and sinks, i.e. the number of molecules with velocity $\mathbf{v}$ at point $\mathbf{r}$, appearing or vanishing per unit time in unit volume and reduced to unit velocity interval. In this case the gas will be assumed to be sufficiently rarified and only binary collisions will be taken into account, ignoring the possibility of simultaneous drawing together for complexes consisting of three, four, etc. molecules. Let us find q_{sour} and q_{sink}.

Let us consider the collisions of molecules, the velocity of one of which lies within the interval $\mathbf{v}$, $\mathbf{v} + d\mathbf{v}$, and of the other within the interval $\mathbf{v}'$, $\mathbf{v}' + d\mathbf{v}'$. Upon collision these molecules acquire the velocities falling within the ranges $\tilde{\mathbf{v}}$, $\tilde{\mathbf{v}} + d\tilde{\mathbf{v}}$ and $\tilde{\mathbf{v}}'$, $\tilde{\mathbf{v}}' + d\tilde{\mathbf{v}}'$ respectively. The number of such collisions per unit time in unit volume is proportional to the number of colliding molecules with velocities within the intervals $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$, $(\mathbf{v}', \mathbf{v}' + d\mathbf{v}')$ and velocity ran-

ges of $d^3\tilde{\mathbf{v}}$ and $d^3\tilde{\mathbf{v}}'$ after collision. This number can be represented in the form

$$P(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' | \mathbf{v}, \mathbf{v}') ff' d^3v d^3v' d^3\tilde{v} d^3\tilde{v}', \tag{85.4}$$

where for the sake of brevity we denote $f \equiv f(\mathbf{r}, \mathbf{v}, t)$, $f' = f(\mathbf{r}, \mathbf{v}', t)$, $P(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' | \mathbf{v}, \mathbf{v}')$ —the probability density of collision $\mathbf{v}, \mathbf{v}' \to \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'$; depending on the velocities of the colliding molecules before and after collision. The total number of collisions experienced by molecules with velocities falling within $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$ per unit time in unit volume is found by integrating over all values of $\mathbf{v}'$, $\tilde{\mathbf{v}}$, $\tilde{\mathbf{v}}'$. Due to the smallness of the interval $d\mathbf{v}$, this expression represents simultaneously the decrease in the number of molecules of this kind.

Thus the strength of the sinks pertinent in Eq. (85.3) is equal to

$$q_{\text{sink}} = \int\int\int P(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' | \mathbf{v}, \mathbf{v}') ff' d^3v' d^3\tilde{v} d^3\tilde{v}'. \tag{85.5}$$

Alongside with the processes $\mathbf{v}, \mathbf{v}' \to \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'$, leading to a decrease in the number of molecules with velocities $\mathbf{v}$, the reverse processes take place in the gas, $\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' \to \mathbf{v}, \mathbf{v}'$, leading to an increase in the number of molecules with velocity $\mathbf{v}$. These processes create sources of a strength

$$q_{\text{sour}} = \int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') \tilde{f}\tilde{f}' d^3v' d^3\tilde{v} d^3\tilde{v}', \tag{85.6}$$

where $P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$ is the transition probability density for $\mathbf{v}, \mathbf{v}' \to \mathbf{v}, \mathbf{v}'$; $f = f(\mathbf{r}, \tilde{\mathbf{v}}, t)$; $f' = f(\mathbf{r}, \tilde{\mathbf{v}}', t)$. It should be emphasized once more that the first argument $\mathbf{r}$ of the distribution function is the same in the expressions for $f, f', \tilde{f}, \tilde{f}'$, since in the instantaneous collision approximation the coordinates are assumed to be invariable during impact, and the difference in the position of the centres of colliding molecules is ignored.

Thus, we obtain for the collision integral

$$J \equiv q_{\text{sour}} - q_{\text{sink}} = \int\int\int [P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') \tilde{f}\tilde{f}' - P(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' | \mathbf{v}, \mathbf{v}') ff'] d^3v' d^3\tilde{v} d^3\tilde{v}'. \tag{85.7}$$

It should be noted that the assumption about the number of collisions being proportional to the product ff', or $\tilde{f}\tilde{f}'$, is based on the assumption that there is no correlation between molecular velocities and it is actually not completely true. In a more rigorous theory the product ff' of $\tilde{f}\tilde{f}'$ must be replaced by the so-called *pair* (or *two-body*) *distribution function* (see the next section).

Let us stipulate some important properties of the function P. We assume that the principle of detailed balancing is valid, meaning from the quantum-mechanical viewpoint that either we consider a

gas of spinless particles, or perform the averaging over the spins of the initial and final states. From the viewpoint of classical mechanics this involves an assumption about the spherical symmetry of gas particles. Even Boltzmann himself indicated that the principle of detailed balancing was not true for particles of non-spherical form. It can readily be seen that, if only one of the colliding particles is not spherical, then a collision with inversion velocities before the impact does not lead in the general case to velocity inversion after the collision.

The principle of detailed balancing is valid with the restriction indicated in the Boltzmann limiting case even in the presence of a time-dependent applied field, since in a "spontaneous" collision approximation the force of interaction during collision must be assumed to be infinitely large, $\mathbf{F} \to \infty$, compared with which the action exerted by the applied field being negligibly small. Thus, the function P is taken to be symmetrical with respect to the permutation of the initial and final state arguments

$$P(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' | \mathbf{v}, \mathbf{v}') = P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'), \tag{85.8}$$

by virtue of which Eq. (85.3) can be reduced to

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial x_k}(f v_k) + \frac{\partial}{\partial v_k}(f w_k) = \int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')\,(\tilde{f}\tilde{f}' - ff')\,d^3v'\,d^3\tilde{v}\,d^3\tilde{v}'. \tag{85.9}$$

Equation (85.9) is called the *Boltzmann transport equation.*

Further, from the very determination of the function P follows its symmetry in the arguments of the first pair, $\mathbf{v}$ and $\mathbf{v}'$, and in the arguments of the second pair, $\tilde{\mathbf{v}}$ and $\tilde{\mathbf{v}}'$, separately:

$$\begin{aligned} P(\mathbf{v}', \mathbf{v} | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') &= P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') \\ P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}', \tilde{\mathbf{v}}) &= P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'). \end{aligned} \tag{85.10}$$

As can be seen from (85.9), Boltzmann's equation is a complicated non-linear integro-differential equation, an approximate solution of which is possible only in some particular cases. However, as will be shown in the following sections, the Boltzmann equation permits us to obtain a number of important corollaries of a rather general nature. Limiting ourselves to the consideration of only elastic collisions and assuming the molecular masses to be the same, let us write down the laws of conservation of momenta and energy during collision in the form

$$\mathbf{v} + \mathbf{v}' = \tilde{\mathbf{v}} + \tilde{\mathbf{v}}', \quad v^2 + (v')^2 = \tilde{v}^2 + (\tilde{v}')^2. \tag{85.11}$$

These equations show the function $P(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$ to contain Dirac's singular multipliers

$$\delta(v_1+v_1'-\tilde{v}_1-\tilde{v}_1')\,\delta(v_2+v_2'-\tilde{v}_2-\tilde{v}_2')\,\delta(v_3+v_3'-\tilde{v}_3-\tilde{v}_3') = \delta(\mathbf{v}+\mathbf{v}'-\tilde{\mathbf{v}}-\tilde{\mathbf{v}}')$$

and

$$\delta(v^2+v'^2-\tilde{v}^2-\tilde{v}'^2), \tag{85.12}$$

ensuring the fulfilment of the conservation laws (85.11) during collision. The collision integral can, therefore, be expressed by the formula

$$J = \int\int\int \Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')(\tilde{f}\tilde{f}' - ff')\,\delta(\mathbf{v}+\mathbf{v}'-\tilde{\mathbf{v}}-\tilde{\mathbf{v}}') \times \delta(v^2+v'^2-\tilde{v}^2-\tilde{v}'^2)\,d^3v'\,d^3\tilde{v}\,d^3\tilde{v}', \tag{85.13}$$

where $\Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$ is the non-singular multiplier in $P[(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$.

It is obvious that $\Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$ possesses the same symmetry properties (85.8) and (85.10) as $P(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$:

$$\begin{aligned} \Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') &= \Pi(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}' \mid \mathbf{v}, \mathbf{v}'), \\ \Pi(\mathbf{v}', \mathbf{v} \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') &= \Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'), \\ \Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}', \tilde{\mathbf{v}}) &= \Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}'). \end{aligned} \tag{85.14}$$

The presence of four δ-functions in formula (85.13) allows an important transformation of the collision integral; four integrations can be performed, reducing, thereby, the nine-fold multiple integral (85.13) to a five-fold one.

Let us denote by $\mathbf{q}$ the relative velocity of particles before collision:

$$\mathbf{q} = \mathbf{v}' - \mathbf{v}. \tag{85.15}$$

Formula (85.11) yields $\tilde{\mathbf{v}} - \mathbf{v} = \mathbf{v}' - \tilde{\mathbf{v}}'$. Introducing the notation $\tilde{\mathbf{v}} - \mathbf{v} = \mathbf{a}$ for particles' velocities after collision, we obtain

$$\tilde{\mathbf{v}} = \mathbf{v} + \mathbf{a}, \quad \tilde{\mathbf{v}}' = \mathbf{v}' - \mathbf{a}. \tag{85.16}$$

Substituting formula (85.16) into (85.11), we get

$$a^2 = \mathbf{qa}. \tag{85.17}$$

Let us present $\mathbf{a}$ in the form $e\boldsymbol{a}$, where $\mathbf{e}$ is a unit vector parallel to $\tilde{\mathbf{v}} - \mathbf{v}$. Then, for the modulus of $\mathbf{a}$ we obtain from (85.17) $a = (\mathbf{qe})$, whence $\mathbf{a} = (\mathbf{qe})\mathbf{e}$ and the velocity of particles after collision can finally be expressed by

$$\tilde{\mathbf{v}} = \mathbf{v} + (\mathbf{qe})\mathbf{e}, \quad \tilde{\mathbf{v}}' = \mathbf{v}' - (\mathbf{qe})\mathbf{e} \tag{85.18}$$

Since expressions (85.18) satisfy the laws of conservation of momentum and energy, their substitution into the collision integral converts into zero the arguments of all δ-functions.

The collision integral can be simplified in the following manner. Let us integrate the right-hand side of (85.13) over $\tilde{\mathbf{v}}'$, making use of the fact that the integrand contains $\delta(\mathbf{v} + \mathbf{v}' - \tilde{\mathbf{v}} - \tilde{\mathbf{v}}')$. We obtain, then, the integral

$$J = \int\int \Pi(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') (\tilde{f}\tilde{f}' - ff') \, \delta(v^2 + v'^2 - \tilde{v}^2 - \tilde{v}'^2) \, d^3v' \, d^3\tilde{v},$$

where $\tilde{\mathbf{v}}'$ in integrand must be expressed in terms of $\mathbf{v}$, $\mathbf{v}'$, $\tilde{\mathbf{v}}$, i.e. $\tilde{\mathbf{v}}' = \mathbf{v} + \mathbf{v}' - \tilde{\mathbf{v}}$. To carry out one more integration using the fact that there is one more δ-function in the integrand, let us pass from the variable $\tilde{\mathbf{v}}$ to the variable vector $R\mathbf{e}$, by the formula

$$\tilde{\mathbf{v}} = \tilde{\mathbf{v}} + R\mathbf{e}(\mathbf{v}, \mathbf{e}). \tag{85.19}$$

It should be noted, comparing (85.19) with (85.18), that actually in the space of vectors $R\mathbf{e}$ only the sphere $R = 1$ contribute to the integral due to the presence of the δ-function. In fact, substituting the values of $\tilde{\mathbf{v}}$ and $\tilde{\mathbf{v}}'$ from formula (85.19), we find for the argument of the δ-function the expression

$$v^2 + v'^2 - \tilde{v}^2 - \tilde{v}'^2 = v^2 + v'^2 - [\mathbf{v} + R\mathbf{e}(\mathbf{qe})]^2 - (\mathbf{v}' - R\mathbf{e}(\mathbf{qe}))^2$$
$$= 2R(\mathbf{qe})^2 (1 - R).$$

The collision integral acquires now the form

$$J = \int\int \Pi(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') \, \delta[2R(\mathbf{qe})^2 (1 - R)] (\tilde{f}\tilde{f}' - ff')$$
$$\times \frac{\partial(\tilde{v}_1, \tilde{v}_2, \tilde{v}_3)}{\partial(R, \theta, \varphi)} R^2 \, dR \, d\Omega \, d^3v'. \tag{85.20}$$

where $d\Omega = \sin\theta \, d\theta \, d\varphi$ is the element of the solid angle for vector $\mathbf{e}$. We could calculate the Jacobian in (85.20) in a simple way, however, as it will be shown below, there is no need in it. Let us integrate over R in Eq. (85.20), using formula (VIII.9):

$$\int F(R) \, \delta[\varphi(R)] \, dR = \sum_i \frac{F(R_i)}{|\varphi'(R_i)|},$$

where R_i are simple roots of equation $\varphi(R_i) = 0$ in the integration region. The collision integral is expressed by the formula

$$J = \int\int \Sigma(\mathbf{v}, \mathbf{v}', \mathbf{e}) (\tilde{f}\tilde{f}' - ff') \, d^3v' \, d\Omega, \tag{85.21}$$

where $\Sigma(\mathbf{v}, \mathbf{v}', \mathbf{e}) = \Sigma(\mathbf{v}, \mathbf{v}', \theta, \varphi)$ denotes the product of the quan-

tity $\Pi(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$ and of all factors appearing when integrating over R, including the Jacobian $\partial(\tilde{v}_1, \tilde{v}_2, \tilde{v}_3)/\partial(R, \theta, \varphi)$. It should be recalled once more that in all the factors of the integrand $\tilde{\mathbf{v}}$ and $\tilde{\mathbf{v}}'$ must be expressed in term of $\mathbf{v}$, $\mathbf{v}'$ and $\mathbf{e}$ in accordance with formulae (85.18).

It follows from the collision theory that the multiplier $\Sigma(\mathbf{v}, \mathbf{v}', \mathbf{e})d\Omega$ is related with the differential scattering cross section $d\sigma(q, \mathbf{e})$, depending, as is known [6], on the interaction potential, relative velocity q and vector $\mathbf{e}$, i.e. on the scattering angle. This relation is expressed by the formula

$$\Sigma(\mathbf{v}, \mathbf{v}', \mathbf{e})d\Omega = q\, d\sigma(q, \mathbf{e}). \tag{85.22}$$

The determination of the effective cross section is a problem of the theory of collision based on the laws of either classical or quantum mechanics. To solve the problem, a concrete particle interaction law must be given. Therefore no explicit universal form of the functions Π and Σ can be given. It is precisely because of this that we gave up calculation of the Jacobian in formula (85.20). Many problems in kinetics can, however, be examined without knowing the explicit form of $\Sigma(\mathbf{v}, \mathbf{v}', \mathbf{e})$. Thus, alongside with Boltzmann's transport equation (85.9), which is more convenient in deriving theorems of a general nature, we have another mathematical description, following from the expression for the collision integral (85.21):

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} = \int\int (\tilde{f}\tilde{f}' - ff')\, q\, d\sigma(q, \mathbf{e})\, d^3v'. \tag{85.23}$$

Problems

1. Write the explicit form of Boltzmann's equation (85.23) for a gas of hard spheres with radius R_0.
2. Show that for molecules interacting according to the law $\mathcal{U} = \alpha/r^4$ (Maxwellian molecules) the product $q\, d\sigma$ is independent of q.

Answer. $d\sigma = \frac{R_0^2}{4} d\Omega = \frac{R_0^2}{4} \sin\theta\, d\theta\, d\varphi$.

§86*. The Bogoliubov Equations

The derivation of Boltzmann's equation outlined in Sec. 85, the idea of which belongs to Boltzmann himself, cannot be assumed to be rigorous. In fact, the presentation of this equation as the continuity equation in the μ-space with sources (collision integral) on the right-hand side presumes, firstly, that the time variation of the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ is additive with respect to two processes that are of different origin. The terms $v_i \partial f/\partial x_i$ and $w_i \partial f/\partial v_i$

on the left-hand side of Eq. (85.9) or (85.2) characterize the fluxes of gas originating due to the existence of a pressure gradient and of applied fields, whereas the right-hand sides appear due to the allowance for molecular collisions. Thus, it is assumed that the fluxes and collisions do not effect on each other. Secondly, the values of the functions f, f', $\tilde{f}$, $\tilde{f}'$ in the collision integral are taken at the same point of space $\mathbf{r}$, whereas, with the account taken of the finite molecular dimensions, different coordinates must be chosen in functions f, f' and $\tilde{f}$, $\tilde{f}'$.

Further, as was already mentioned, the classical derivation of Boltzmann's equation presumes the absence of correlation between molecular velocities. Finally, which is most essential, Boltzmann's equation accounts only for binary molecular collisions, and no more or less clear recipe exists that would account for the collisions of groups consisting of three, four and more molecules. It is meanwhile clear that an allowance for such processes is essential for dense gases.

In a binary collision approximation the mean free path is inversely proportional to gas density:

$$\lambda_0 = 1/\sigma n = \omega/\sigma$$

where σ is the effective cross section of binary collisions.

As is known, this leads to that the transport coefficients $\varkappa$ (thermal conductivity) and α (viscosity) are independent of density n and, consequently, of pressure. Allowing for many-particle collisions, the expression for λ must be of the form

$$\lambda = \frac{1}{\sigma n + \alpha n^2 + \beta n^3 + \ldots} = \lambda_0 \left[1 + \frac{A}{\omega} + \frac{B}{\omega^2} + \ldots \right],$$

where the coefficients α, A and β, B appear due to the account of triple and quadraple collisions respectively, etc. As a result there must appear for the mean free path and for the transport coefficients the virial expansions of the type appearing in statistical physics for the equation of state of a non-ideal gas (see Sec. 58).

In connection with the foregoing a more strict approach is expedient to the problem concerning the derivation of the transport equation and to its possible generalizations. This can be accomplished with the aid of the very general and rigorous method due to N.N. Bogoliubov [38], [39], which will outlined briefly below.

Let us consider a system of N identical particles, the state of which will be given in classical mechanics with the aid of $2N$ vectors $\mathbf{r}_i$, $\mathbf{v}_i$. For the sake of brevity the totality of $\mathbf{r}_i$ and $\mathbf{v}_i$ will be denoted by the symbol x_i, and the product $d^3r_i d^3v_i$ by the symbol dx_i. We introduce the distribution function $F^{(N)}(x_1, \ldots, x_N, t)$ in the Γ-space assuming that the coordinates of the $6N$-dimensional Γ-space are the velocity coordinates and projections for all particles. The ex

pression

$$F^{(N)}(x_1, x_2, \ldots, x_N, t)\, dx_1 dx_2 \ldots dx_N$$

is the probability of finding a Γ-space representative point in volume $dx_1 dx_2 \ldots dx_N$, and that the function $F^{(N)}$ is normalized to unity:

$$\int F^{(N)}(x_1, x_2, \ldots, x_N, t)\, dx_1 dx_2 \ldots dx_N = 1. \qquad (86.1)$$

It will be assumed below that applied fields are absent and that particles interact with an interaction potential $\mathcal{U}(r_{ik}) = mu(r_{ik})$, the properties of which have been discussed in Sec. 65. To eliminate boundary effects, a thermodynamic limit will be considered when $N \to \infty$, $V \to \infty$, and $\omega = V/N$ remains finite.

Further reasonings are based on the Liouville equation derived in Sec. 60 and presented here in the form

$$\frac{\partial F^{(N)}}{\partial t} + \hat{L}_N F^{(N)} = 0, \qquad (86.2)$$

where the operator $\hat{L}^{(N)}$, called *Liouville's operator*, is determined by the formula

$$L_N = \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_i \mathbf{w}_i \frac{\partial}{\partial \mathbf{v}_i} = \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i,\, k \neq i} \mathbf{w}_{i,k} \frac{\partial}{\partial \mathbf{v}_i}, \qquad (86.3)$$

with $\mathbf{w}_{ik} = -\partial u(r_{ik})/\partial \mathbf{r}_i$ being the acceleration imparted to the ith particle due to interaction with the kth particle. The distribution functions $\rho(p, q)$ examined in Sec. 60 and the functions $f^{(N)}(\mathbf{r}_i, \mathbf{v}_i, t)$ in this section are in essence identical and, therefore, the function $F^{(N)}(x_i, t)$ obeys Eq. (60.10). The reader's attention is drawn to the following fundamental properties of Liouville's equation

1. The function $F^{(N)}(x_1, x_2, \ldots, x_N, t)$ was only "forcibly" associated by us with probability notions. We could consider the function not as the probability density for a unit system with coordinates $\mathbf{r}_i$, $\mathbf{v}_i$, but as the distribution function arbitrarily given at the initial instant of time for an ensemble of systems—the Gibbs ensemble.

In other words, we can imagine that at $t = 0$ we are "preparing" an ensemble, i.e. "pour" in an arbitrary manner the representative points into the phase space, setting, thereby, $F^{(N)}(x_1, \ldots, x_N, 0)$. Later on these "poured out" points "float" along their phase trajectories obeying only the laws of mechanics. Thus, Eq. (86.2) has no statistical probabilistic content and carries only purely mechanical information.

2. Liouville's equation, being a first-order equation in time, describes the causal change in the function $F^{(N)}(x_1, \ldots, x_N, t)$. If we have the initial value of the function $F^{(N)}(x_1, \ldots, x_N, 0)$, (86.2) predicts unambiguously all future values of $F^{(N)}(x_i, t)$.

on the left-hand side of Eq. (85.9) or (85.2) characterize the fluxes of gas originating due to the existence of a pressure gradient and of applied fields, whereas the right-hand sides appear due to the allowance for molecular collisions. Thus, it is assumed that the fluxes and collisions do not effect on each other. Secondly, the values of the functions f, f', $\tilde{f}$, $\tilde{f}'$ in the collision integral are taken at the same point of space r, whereas, with the account taken of the finite molecular dimensions, different coordinates must be chosen in functions f, f' and $\tilde{f}$, $\tilde{f}'$.

Further, as was already mentioned, the classical derivation of Boltzmann's equation presumes the absence of correlation between molecular velocities. Finally, which is most essential, Boltzmann's equation accounts only for binary molecular collisions, and no more or less clear recipe exists that would account for the collisions of groups consisting of three, four and more molecules. It is meanwhile clear that an allowance for such processes is essential for dense gases.

In a binary collision approximation the mean free path is inversely proportional to gas density:

$$\lambda_0 = 1/\sigma n = \omega/\sigma$$

where σ is the effective cross section of binary collisions.

As is known, this leads to that the transport coefficients $\varkappa$ (thermal conductivity) and α (viscosity) are independent of density n and, consequently, of pressure. Allowing for many-particle collisions, the expression for λ must be of the form

$$\lambda = \frac{1}{\sigma n + \alpha n^2 + \beta n^3 + \ldots} = \lambda_0 \left[1 + \frac{A}{\omega} + \frac{B}{\omega^2} + \ldots \right],$$

where the coefficients α, A and β, B appear due to the account of triple and quadraple collisions respectively, etc. As a result there must appear for the mean free path and for the transport coefficients the virial expansions of the type appearing in statistical physics for the equation of state of a non-ideal gas (see Sec. 58).

In connection with the foregoing a more strict approach is expedient to the problem concerning the derivation of the transport equation and to its possible generalizations. This can be accomplished with the aid of the very general and rigorous method due to N.N. Bogoliubov [38], [39], which will outlined briefly below.

Let us consider a system of N identical particles, the state of which will be given in classical mechanics with the aid of $2N$ vectors $\mathbf{r}_i$, $\mathbf{v}_i$. For the sake of brevity the totality of $\mathbf{r}_i$ and $\mathbf{v}_i$ will be denoted by the symbol x_i, and the product $d^3r_i d^3v_i$ by the symbol dx_i. We introduce the distribution function $F^{(N)}(x_1, \ldots, x_N, t)$ in the Γ-space assuming that the coordinates of the $6N$-dimensional Γ-space are the velocity coordinates and projections for all particles. The ex

pression

$$F^{(N)}(x_1,\ x_2,\ \ldots,\ x_N,\ t)\,dx_1\,dx_2\ \ldots\ dx_N$$

is the probability of finding a Γ-space representative point in volume $dx_1\,dx_2\ \ldots\ dx_N$, and that the function $F^{(N)}$ is normalized to unity:

$$\int F^{(N)}(x_1,\ x_2,\ \ldots,\ x_N,\ t)\,dx_1\,dx_2\ \ldots\ dx_N = 1. \qquad (86.1)$$

It will be assumed below that applied fields are absent and that particles interact with an interaction potential $\mathcal{U}(r_{ik}) = mu(r_{ik})$, the properties of which have been discussed in Sec. 65. To eliminate boundary effects, a thermodynamic limit will be considered when $N \to \infty$, $V \to \infty$, and $\omega = V/N$ remains finite.

Further reasonings are based on the Liouville equation derived in Sec. 60 and presented here in the form

$$\frac{\partial F^{(N)}}{\partial t} + \hat{L}_N F^{(N)} = 0, \qquad (86.2)$$

where the operator $\hat{L}^{(N)}$, called *Liouville's operator*, is determined by the formula

$$\hat{L}_N = \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_i \mathbf{w}_i \frac{\partial}{\partial \mathbf{v}_i} = \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i,\ k \neq i} \mathbf{w}_{i,\ k} \frac{\partial}{\partial \mathbf{v}_i}, \qquad (86.3)$$

with $\mathbf{w}_{ik} = -\partial u(r_{ik})/\partial \mathbf{r}_i$ being the acceleration imparted to the ith particle due to interaction with the kth particle. The distribution functions $\rho(p, q)$ examined in Sec. 60 and the functions $f^{(N)}(\mathbf{r}_i,\ \mathbf{v}_i, t)$ in this section are in essence identical and, therefore, the function $F^{(N)}(x_i, t)$ obeys Eq. (60.10). The reader's attention drawn to the following fundamental properties of Liouville's equation

1. The function $F^{(N)}(x_1, x_2, \ldots, x_N, t)$ was only "forcibly" associated by us with probability notions. We could consider the function not as the probability density for a unit system with coordinates $\mathbf{r}_i$, $\mathbf{v}_i$, but as the distribution function arbitrarily given at the initial instant of time for an ensemble of systems—the Gibbs ensemble.

In other words, we can imagine that at $t = 0$ we are "preparing" an ensemble, i.e. "pour" in an arbitrary manner the representative points into the phase space, setting, thereby, $F^{(N)}(x_1, \ldots, x_N, 0)$. Later on these "poured out" points "float" along their phase trajectories obeying only the laws of mechanics. Thus, Eq. (86.2) has no statistical probabilistic content and carries only purely mechanical information.

2. Liouville's equation, being a first-order equation in time, describes the causal change in the function $F^{(N)}(x_1, \ldots, x_N, t)$. If we have the initial value of the function $F^{(N)}(x_1, \ldots, x_N, 0)$, (86.2) predicts unambiguously all future values of $F^{(N)}(x_i, t)$.

3. Just as any other equation of classical mechanics, Liouville's equation is reversible in time, meaning that when t is replaced by $-t$, the equation does not change. Hence, along with "direct" motion of copies of the emsemble, "reverse" motion is equally possible upon a corresponding change in the initial conditions.

4. In the light of what was said in item 1, no wonder that a solution of Liouville's equation is equivalent to that of a problem in dynamics, i.e. to finding all dynamic trajectories. Formally this is clear from that the characteristics of Eq. (86.2) have the form $\frac{dt}{1} = \frac{d\mathbf{r}_i}{\mathbf{v}_i} = \frac{d\mathbf{v}_i}{\mathbf{w}_i}$, from which follow the equations of dynamics in Newton's form:

$$m\frac{d^2\mathbf{r}_i}{dt^2} = m\frac{d\mathbf{v}_i}{dt} = m\mathbf{w}_i = -m\sum_{k\neq i}\frac{\partial \mathbf{u}(\mathbf{r}_{ik})}{\partial \mathbf{r}}.$$

Physically, it follows from the fact that we can "prepare" an initial ensemble in the form $F^{(N)}(x_i, 0) = \prod_i \delta(x_i - x_i^{(0)})$, i.e. "point out" all representative points into one point of the phase space. By virtue of the fact that the solution of Liouville's equation is unambiguous for the given initial conditions, the motion of the representative point describes the evolution of only one dynamic system. Thus, along with the methods of solution for problems in dynamics based on the integration of the Newton, Lagrange, Hamilton and Hamilton-Jacoby equations, there exists one more method the method of integrating Liouville's equation. For a system with an enormous number of particles this method is, however, as unsuitable and unnecessary as all the other methods, and problems in macroscopic non-equilibrium physics must be solved applying probability methods.

For this purpose let us introduce the n-particle distribution functions

$$V^{-n}F_n^{(N)}(x_1, x_2, \ldots, x_n, t) = \int F^{(N)}(x_1, x_2, \ldots, x_N, t)\, dx_{n+1} \ldots dx_N. \quad (86.4)$$

These functions obey the normalization conditions stemming from Eq. (86.1);

$$V^{-n}\int F_n^{(N)}(x_1, x_2, \ldots, x_n, t)\, dx_1 dx_2 \ldots dx_n = 1 \quad (86.5)$$

and, if we impart a probability meaning to the function $F^{(N)}(x_1, \ldots, x_N, t)$, the functions $V^{-n}F_n(x_1, \ldots, x_n, t)$ also acquire a statistical interpretation. For the sake of brevity the superscript (N) is omitted in the notation of $F_n^{(N)}$ here and below. The expression V^{-n}

$F_n(x_1, \ldots, x_n, t)$ is the probability that the first n particles of a system (and not of an ensemble of systems) have coordinates and velocities falling within $(\mathbf{r}_i, \mathbf{r}_i + d\mathbf{r}_i)$, $(\mathbf{v}_i, \mathbf{v}_i + d\mathbf{v}_i)$.

Let us derive a system of differential equations governing the functions $F_n(x_1, \ldots, x_n, t)$, multiplying for this purpose Eq. (86.2) by $V^n dx_{n+1} \ldots dx_N$ and integrating the equality obtained, using (86.3):

$$\frac{\partial F_n(x_1, \ldots, x_n, t)}{\partial t} + \sum_{i=1}^{n} \frac{\partial}{\partial \mathbf{r}_i} [F_n(x_1, \ldots, x_n, t)\, \mathbf{v}_i]$$

$$+ \frac{1}{V} \sum_{i=n+1}^{N} \int \frac{\partial}{\partial \mathbf{r}_i} [F_{n+1}(x_1, \ldots, x_n, x_i, t)\, \mathbf{v}_i]\, dx_i$$

$$+ \sum_{i=1}^{n} \sum_{k=1}^{n} \frac{\partial}{\partial \mathbf{v}_i} [F_n(x_1, \ldots, x_n, t)\, \mathbf{w}_{ik}]$$

$$+ \frac{1}{V} \sum_{i=1}^{n} \sum_{k=n+1}^{N} \frac{\partial}{\partial \mathbf{v}_i} \int F_{n+1}(x_1, \ldots, x_n, x_k, t)\, \mathbf{w}_{ik}\, dx_k$$

$$+ \frac{1}{V} \sum_{i=n+1}^{N} \sum_{k=1}^{n} \int \frac{\partial}{\partial \mathbf{v}_i} [F_{n+1}(x_1, \ldots, x_n, x_i, t)\, \mathbf{w}_{ik}]\, dx_i$$

$$+ \frac{1}{V^2} \sum_{i=n+1}^{N} \sum_{k=n+1}^{N} \int\int \frac{\partial}{\partial \mathbf{v}_i} [F_{n+2}(x_1, \ldots, x_n, x_i, x_k, t)\, \mathbf{w}_{ik}]$$

$$\times dx_i\, dx_k = 0. \quad (86.6)$$

It should be noted now that in Eq. (86.6) the third, sixth and seventh terms are equal to zero identically. In fact, each of these terms is an integral of a three-dimensional divergence: the third term—in the coordinate space of the ith molecule, the sixth and seventh—in the velocity space of the ith molecule. According to the Gauss theorem, they can be transformed into an integral over the boundary surface. The function F_n, however, vanishes when the coordinates of any gas particle correspond to points lying on the absolutely impermeable wall of a vessel and, on the other hand, the distribution function F_n tends to zero as $v_i \to \infty$. For this reason the integral of the divergence is equal to zero both in the coordinate space and in the velocity space. On the other hand, the fifth term in Eq. (86.5) can be transformed in the following way. The individual terms in the sum

over k differ only in the notation of the integration variable:

$$\frac{1}{V}\sum_{i=1}^{n}\sum_{k=n+1}^{N}\frac{\partial}{\partial \mathbf{v}_i}\int F_{n+1}(x_1, \ldots, x_n, x_k, t)\,\mathbf{w}_{ik}\,dx_k$$

$$= \frac{N-n}{V}\sum_{i=1}^{n}\frac{\partial}{\partial \mathbf{v}_i}\int F_{n+1}(x_1, \ldots, x_{n+1}, t)\,\mathbf{w}_{i,\,n+1}\,dx_{n+1}.$$

Thus, we finally obtain a system of equations

$$\frac{\partial F_n(x_1, x_2, \ldots, x_n, t)}{\partial t} + \hat{L}_n F_n(x_1, x_2, \ldots, x_n, t)$$

$$= -\frac{N-n}{V}\sum_{i=1}^{n}\int \mathbf{w}_{i,\,n+1}\frac{\partial F_{n+1}(x_1, \ldots, x_{n+1}, t)}{\partial \mathbf{v}_i}\,dx_{n+1}. \qquad (86.7)$$

In the literature this system is usually referred to as the *BBKGI* (Born, Bogoliubov, Kirkwood, Green, Ivon) *hierarhy*. Below, for the sake of brevity, we shall call it the *Bogoliubov system of equations* because the most detailed analysis of this system of equations was given by Bogoliubov. The factor $\hat{L}_n$ in formula (86.7) is the Liouville operator for a subsystem of n particles. The Bogoliubov system of equations is of the "linked" kind, since the equations for the function F_n contain on the right-hand side the function F_{n+1}. From the physical viewpoint it reflects the fact that any group of n molecules ($n < N$), interacting with the other $N-n$ molecules, is open. As is clear from (86.7), Liouville's operator determines unambiguously the time evolution of function $F_n(x_1, \ldots, x_n, t)$ for a closed system of particles, whereas the right-hand side of this formula describes its open nature.

It should be noted that the last equation in system (86.7) for the function F_N is closed and identical to Liouville's equation (86.2). From the mathematical viewpoint, integration of the system of equations (86.7) should be initiated by integration this equation. In doing so, naturally, it would not be necessary to integrate the remaining $N-1$ equations of the system, since all n-particle distribution functions can be found by formulae (86.4) after the function $F_N(x_1, \ldots, x_N, t)$ is identified, and the system would become unnecessary at all. However, as has been already mentioned, integration of Liouville's equation is practically impossible.

Thus, the physically reasonable method of solving the Bogoliubov system of equations consists in initiating this procedure not from the last equation for the function F_N, but from the first for the function F_1, and in trying to "break" system (86.7) in some way. If it happens to be possible to express some function F_{n+1} as a functional of functions F_l ($l \leqslant n$), then it becomes possible to "break" system (86.7)

and we arrive to a system with a finite number of equations. In particular, if it proves possible to express in some way the function $F_2(x_1, x_2, t)$ as a functional of $F_1(x_1, t)$, we obtain the equation for the one-particle function $F_1(x_1, t)$, generally called the *kinetic equation*. The Boltzmann equation and the Fokker-Planck equation are particular cases of kinetic equations.

We pay much attention to the one-particle and two-particle functions $F_1(x_1, t)$ and $F_2(x_1, x_2, t)$ for the following reasons. The one-particle function can be used to express the quantities that are important in gas dynamics, such as the mean particle density $n(\mathbf{r}, t)$, the mean particle flux velocity $\mathbf{u}(\mathbf{r}, t)$, and the mean kinetic energy $3/2\ T(\mathbf{r}, t)$, which are determined by the formulae

$$n(\mathbf{r}, t) = \frac{N}{V} \int d^3v\, F_1(\mathbf{r}, \mathbf{v}, t), \tag{86.8}$$

$$n(\mathbf{r}, t)\, \mathbf{u}(\mathbf{r}, t) = \frac{N}{V} \int d^3v\, \mathbf{v} F_1(\mathbf{r}, \mathbf{v}, t), \tag{86.9}$$

$$n(\mathbf{r}, t)\, U(\mathbf{r}, t) = \frac{3}{2} n(\mathbf{r}, t)\, T(\mathbf{r}, t)$$

$$= \frac{N}{V} \int d^3v \frac{mv^2}{2} F_1(\mathbf{r}, \mathbf{v}, t). \tag{86.10}$$

It will be shown below that other important quantities in gas dynamics, such as the viscous force tensor and heat flux, are also expressed in terms of one-particle distribution functions. The two-particle distribution function is of paramount importance for the equilibrium state of a system. In the equilibrium state it describes the correlations between the position of particles, which were shown in Sec. 81 to be of great importance in the theory of fluctuations and in the theory of phase transitions.

It should be noted, finally, that the probability meaning was forcibly" attributed to the definition of the n-particle functions $F_n(x_1, \ldots, x_n, t)$ and $F^{(N)}(x_1, \ldots, x_N, t)$, and we obtained, in principle, the system of equations (86.7) fully equivalent to Liouville's equation without associating in any way the functions F_n with the probability characteristics of a unit system. It follows from this that the system of equations (86.7) is a system of mechanical and not statistical equations. No wonder, therefore, that this system, just as Liouville's equation, is invariant in respect to time reflection, i.e. to the replacement of t by $-t$, and it cannot describe irreversible macroscopic processes. Irreversibility will be shown in Secs. 87, 96 to be introduced into the formalism of the theory only by certain hypotheses of a particularly probability nature.

Let us write in the explicit form the equations for F_1 and F_2, which will be dealt with in greater detail below, neglecting the term

$n = 1, 2$ in the factor $(N - n)/V$ pertinent in system (86.7):

$$\frac{\partial F_1(x_1, t)}{\partial t} + \hat{L}_1 F_1(x_1, t) = -\frac{1}{\omega}\int w_{12}\frac{\partial F_2(x_1, x_2, t)}{\partial v_1}\,dx_2, \quad (86.11)$$

$$\frac{\partial F_2(x_1, x_2, t)}{\partial t} + \hat{L}_2 F_2(x_1, x_2, t)$$

$$= -\frac{1}{\omega}\int\left[w_{13}\frac{\partial F_3(x_1, x_2, x_3, t)}{\partial v_1} + w_{23}\frac{\partial F_3(x_1, x_2, x_3, t)}{\partial v_2}\right]dx_3, \quad (86.12)$$

where

$$\hat{L}_1 = v_1\frac{\partial}{\partial r_1}, \quad (86.13)$$

$$\hat{L}_2 = v_1\frac{\partial}{\partial r_1} + v_2\frac{\partial}{\partial r_2} + w_{12}\frac{\partial}{\partial v_1} + w_{21}\frac{\partial}{\partial v_2}. \quad (86.14)$$

Problem

Introduce a radial distribution function connected with function $F_2(x_1, x_2, t)$ by the relationship $g(|r_1 - r_2|) = (V/N)^2\int F_2\,d^3v_1\,d^3v_2$ and show that in the equilibrium state the equation of state is expressed by the formula

$$\frac{PV}{NT} = 1 - \frac{2\pi N}{3VT}\int_0^\infty r^3 g(r)\frac{\partial u(r)}{\partial r}\,dr,$$

where $u(r)$ is a two-particle potential.

87*. Evolution Stages for a Non-Equilibrium System. Bogoliubov's Derivation of Boltzmann's Equation

Let us now show how the Boltzmann equation can be derived from the system of equations (86.7) (this derivation is due to N.N. Bogoliubov). A gas is assumed to be so rarified that

$$\frac{r_0^3}{\omega} \sim \frac{r_0}{\lambda} \ll 1, \quad (87.1)$$

where r_0 is the range of interaction, and λ is the mean free path. The right-hand side of Eqs. (86.7) contains terms of the order of magnitude of r_0^3/ω, since owing to the factor $w_{i,n+1} = -\partial u(r_{i,n+1})/\partial r_i$ the integration with respect to coordinates is carried out over the volume approximately equal to r_0^3.

The method of solving system (86.7) by expanding in the small parameter r_0^3/ω turns out to be all the same insufficient. To explain the reason for such insufficiency, let us introduce three characteristic times: effective duration of collisions $\tau_0 \sim r_0/\bar{v}$, mean interval be-

tween collisions τ,

$$\tau \sim \frac{\lambda}{\bar{v}} \sim \frac{\omega}{r_0^3} \frac{r_0}{\bar{v}} \gg \tau_0,$$

and the macroscopic relaxation time T^*, which differs for various physical problems, but is, as a rule, much greater than τ. The last condition assumes that the gas is sufficiently rarified, for the condition $\lambda \gg r_0$ to be fulfilled, but at the same time so dense that $\lambda < L$ (L is the size of the vessel). Otherwise, we are dealing with a Knudsen gas (flow) in which the molecules collide only with the walls of the vessel and not with each other. This case will not be treated here. Thus, we have the inequalities

$$r_0 \ll \lambda < L, \quad \tau_0 \ll \tau < T^*. \tag{87.2}$$

As is seen from Eq. (86.11), describing the time variation of the function F_1, in the zeroth approximation with respect to parameter r_0^3/ω this equation does not contain the intramolecular force potential $u(r_{ik})$. This means that in time intervals of the order of τ_0 the function F_1 experiences no essential changes due to molecular interactions (collisions) and it can be approximately assumed to be constant. However, the analysis of the correction term on the right-hand side of Eq. (86.11) shows (see [38]) that in a time interval of the order of τ the changes in the function F_1 become already considerable, and the expansion in r_0^3/ω ceases to be sufficient.

In contrast to this, Eq. (86.12), describing the time evolution of the function F_2 [and, in general, Eqs. (86.7) at $n \geqslant 2$] contains the intermolecular force potential even in the zeroth approximation with respect to parameter r_0^3/ω. It is present in the terms $w_{ik}(\partial F_n/\partial v_i)$ of the Liouville operator $\hat{L}_n$, which leads to "rapid" changes of the functions F_2, F_3, ... in a time interval of the order of τ_0. On a "rough" time scale, accounting only for the changes during time intervals $t \gtrsim \tau$, these rapid changes in function F_n are averaged and only a smooth evolution of these functions remains. It seems to be rather plausible to assume that the slow evolution of many-particle distribution functions, following the initial stage of rapid randomization in time τ_0, is fully determined by the slow evolution of the one-particle function $F_1(x, t)$. In fact, after several collisions have occurred in the system, the behaviour of molecules becomes "unified" and the one-particle function gives sufficiently complete information on the system.

Thus, the initial non-equilibrium state of the system changes in time, passing through a succession of stages.

1. $t \sim \tau_0$. The stage of *initial randomization*. In this stage the state can be adequately described in the general case only by a complete N particle distribution function $F_N(x_1, \ldots, x_N, t)$. In fact, the transition to a one-particle, two-particle and, in general, n-particle

distribution function, implying an averaging (integration in (86.4)) over molecular coordinates and velocities, eliminates the information on the nature of the state. If the initial state originated, for instance, as a result of a delivery of a beam of fast molecules into a cold gas with the Maxwellian velocity distribution, then integration over velocities and coordinates should "erase" the only important information on the presence of two groups of "hot" and "cold" molecules.

2. $\tau_0 \ll t \leqslant \tau$. Bogoliubov called this stage *kinetic* and in this stage the knowledge of the one-particle distribution function is sufficient to characterize the state of a gas. As we have seen, however, in the problem for Sec. 86, the solution of some more delicate problems, finding the equation of state, for instance, requires the knowledge of the two-particle function of state as well.

3. $\tau < t$. This stage, called *hydrodynamic*, is characterized by the fact that after several collisions occur, *local equilibrium* sets in in small volumes of the gas (see Sec. 92). We shall see below (Sec. 94) that in such quasi-equilibrium states, to describe the system it is even not necessary to know the one-particle distribution function; the knowledge of the several first momenta of function $f(\mathbf{r}, \mathbf{v}, t)$ is sufficient for the purpose.

By the momenta of the function f will be meant the integrals of function $f(\mathbf{r}, \mathbf{v}, t)$ over the velocity space with the weights that are products of velocity projections. The zero momentum, for instance,

$$\int d^3v f(\mathbf{r}, \mathbf{v}, t)$$

is the spatial particle density $n(\mathbf{r}, t)$; the first momentum

$$\int d^3v v_i f(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t)\, u_i(\mathbf{r}, t)$$

defines the mean macroscopic velocity, etc.

Let us examine in greater detail the kinetic stage of evolution. The method of interpreting the system of equations (86.7) for this stage, suggested by Bogoliubov, consists in the following.

Firstly, all many-particle distribution functions are assumed to depend on time only through the function $F_1(y, t)$:

$$F_n(x_1, \ldots, x_n, t) = F_n[x_1, \ldots, x_n | F_1(y, t)], \quad n \geqslant 2. \qquad (87.3)$$

It should be noted that the function $F_n(x_1, \ldots, x_n \mid F_1)$ does not depend on the argument y of the function $F_1(y, t)$ (we denote on purpose the first argument of the function F_1 by the symbol y to avoid the danger of confusing it with one of the arguments $x_1, \ldots, x_n$). Each function $F_1(y, t)$ is associated with the numerical function $F_n(x_1, \ldots, x_n, t)$, depending parametrically on $x_1, \ldots, x_n$ and t and independent of y. Such dependence is said to be functional, and the function F_n itself is referred to as the functional of F_1. In formula

(87.3) and in all the following formulae the functional argument F_1 is separated from the ordinary arguments $x_1, \ldots, x_n$ by a vertical line and for the sake of brevity the arguments of the function F_1 will often be omitted.

It can be demonstrated that the most general form of the functional dependence of an arbitrary function $\psi(x_1, \ldots, x_n \mid F_1)$ on F_1 is given by the formula

$$\psi(x_1, \ldots, x_n | F_1) = \int A(x_1, \ldots, x_n, y)\, \Phi[F_1(y, t)]\, dy, \quad (87.4)$$

where $A(x_1, \ldots, x_n, y)$ and $\Phi(F_1)$ are some arbitrary functions of their arguments, such that the integral in Eq. (87.4) exists.

Secondly, at $n \geqslant 2$ the function $F_n(x_1, \ldots, x_n \mid F_1)$ [and not the function $F_1(y, t)$] are represented by virial power expansions in $1/\omega$. These expansions are actually carried out in powers of the dimensionless parameter r_0^3/ω, but it is formally more convenient to write them as expansions in $1/\omega$:

$$F_n(x_1, \ldots, x_n | F_1) = F_n^{(0)}(x_1, \ldots, x_n | F_1) + \frac{1}{\omega} F_n^{(1)}(x_1, \ldots, x_n | F_1) + \ldots . \quad (87.5)$$

We pass now to deriving the equation describing the slow evolution of the function $F_1(x, t)$—the kinetic equation. Substituting the virial expansion (87.5) for the function $F_2(x_1, x_2 \mid F_1)$ into the right-hand side of Eq. (86.11), we obtain

$$\frac{\partial F_1(x_1, t)}{\partial t} + \hat{L}_1 F_1(x_1, t) = -\frac{1}{\omega} \int w_{12} \frac{\partial F_2^{(0)}(x_1, x_2 | F_1)}{\partial v_1} dx_2 - \frac{1}{\omega^2} \int w_{12} \frac{\partial F_2^{(1)}(x_1, x_2 | F_1)}{\partial v_1} dx_2 + \ldots . \quad (87.6)$$

In this way we shall obtain the kinetic equation to the first order in r_0^3/ω, if we find the functional dependence of $F_2^{(0)}$ on F_1; to the second order in r_0^3/ω if we find the functional dependence of $F_2^{(1)}$ on F_1, and, in general, to the kth order in r_0^3/ω if we find the functional dependence of $F_2^{(k-1)}$ on F_1. Let us derive the kinetic equation to the first order in r_0^3/ω, outlining the way of finding the next terms as well. We refer the readers who are interested in a more detailed treatment of the subject to the monographs [38], [39] and to the papers (a rather complete list of such papers is given in [39]).

Substituting into Eq. (86.12) expansion (87.5), we obtain for the function $F_2^{(0)}(x_1, x_2 \mid F_1)$ the equation

$$\left(\frac{\partial}{\partial t} + \hat{L}_2\right) F_2^{(0)}(x_1, x_2 | F_1) = 0. \quad (87.7)$$

Equation (87.7) can be only formally taken for a differential equation; actually it is a functional equation. In fact, in accordance

with the main hypothesis (87.3) and the definition (87.4), we must substitute into Eq. (87.7) the expression (87.4) for $F_2^{(0)}$,

$$F_2^{(0)}(x_1, x_2|F_1) = \int A(x_1, x_2, y)\,\Phi[F_1(y, t)]\,dy, \qquad (87.8)$$

and for the derivative $\partial F_2^{(0)}/\partial t$ the expression

$$\frac{\partial F_2^{(0)}}{\partial t} = \int A(x_1, x_2, y)\,\Phi'[F_1(y, t)]\,\frac{\partial F_1}{\partial t}\,dy, \qquad (87.9)$$

where the symbol Φ' denotes the derivative of the function Φ with respect to its argument F_1. Using Eq. (87.6) written in the zeroth approximation in $1/\omega$,

$$\frac{\partial F_1}{\partial t} + \hat{L}_1 F_1 = 0,$$

we rewrite Eq. (87.9) also in the form

$$\frac{\partial F_2^{(0)}}{\partial t} = -\int A(x_1, x_2, y)\,\Phi'[F_1(y, t)]\,\hat{L}_1 F_1(y, t)\,dy. \qquad (87.10)$$

Let us show, following the Bogoliubov method, how the functional equation (87.7) can be converted into a differential one. For this purpose we introduce the dynamic displacement operator for time τ in a closed system of n particles, $\hat{S}_n(x_1, \ldots, x_n, \tau)$:

$$\hat{S}_n(x_1, \ldots, x_n, \tau) = e^{\tau \hat{L}_n(x_1, \ldots, x_n)}. \qquad (87.11)$$

In this case by the exponential function of operator $\hat{L}_n$ is meant a Maclaurin series for this function:

$$e^{\tau \hat{L}_n} = 1 + \tau \hat{L}_n + \frac{\tau^2}{2!}\hat{L}_n^2 + \ldots .$$

It should be noted that since the operator terms $\hat{L}_n$ do not commute with each other, for instance, $\mathbf{v}_i \partial/\partial \mathbf{r}_i$ and $\mathbf{w}_{km}\partial/\partial \mathbf{v}_k$ at $k = i$ or $m = i$, the exponential $e^{\tau \hat{L}_n}$ cannot be presented as the product of exponentials corresponding to the terms $\hat{L}_n$.

The operators $\hat{S}_n(\tau)$ possess the property consisting in that, when acting on the coordinates and velocities $\mathbf{r}_i$ and $\mathbf{v}_i$ ($i = 1, 2, \ldots, n$) of a system of n particles at the instant of time t, they transform them into coordinates and velocities at the instant of time $t + \tau$ provided that the system is closed. In fact, for instance, for the operator $\hat{S}_1(\tau)$ we have

$$\hat{L}_1 \mathbf{r}_1 = \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1}\mathbf{r}_1 = \mathbf{v}_1, \quad \hat{L}_1^2 \mathbf{r}_1 = \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1}\mathbf{v}_1 = 0, \quad \hat{L}_1 \mathbf{v}_1 = 0,$$

whence

$$\hat{S}_1(\tau)\,\mathbf{r}_1 = e^{\tau \hat{L}_1}\mathbf{r}_1 = (1 + \tau \hat{L}_1)\,\mathbf{r}_1 = \mathbf{r}_1 + \mathbf{v}_1 \tau,$$

$$\hat{S}_1(\tau)\,\mathbf{v}_1 = e^{\tau \hat{L}_1}\mathbf{v}_1 = \mathbf{v}_1.$$

For one isolated particle the velocity is the integral of motion and the motion of this particle is uniform, so that

$$\hat{S}_1(\tau)\,\psi(\mathbf{r}_1,\ \mathbf{v}_1,\ t)=\psi(\mathbf{r}_1+\mathbf{v}_1\tau,\ \mathbf{v}_1,\ t).$$

For the operator $\hat{S}_n(\tau)$ with an arbitrary $n \geqslant 1$ we have

$$\hat{L}_n=\sum_{i=1}^{n}\mathbf{v}_i\frac{\partial}{\partial\mathbf{r}_i}+\sum_{i=k=1}^{n}\mathbf{w}_i\frac{\partial}{\partial\mathbf{v}_i}=\sum_{i=1}^{n}\left[\frac{d\mathbf{r}_i}{dt}\frac{\partial}{\partial\mathbf{r}_i}+\frac{d\mathbf{v}_i}{dt}\frac{\partial}{\partial\mathbf{v}_i}\right]$$

$$=\sum_{i=1}^{n}\frac{dx_i}{dt}\frac{\partial}{\partial x_i},$$

and, consequently, for the small time interval $\delta\tau$ we obtain

$$(1+\delta\tau\hat{L}_n)\,\psi(x_1,\ \ldots,\ x_n,\ t)=\psi(x_1+\delta x_1,\ \ldots,\ x_n+\delta x_n,\ t).$$

In the above relation δx_i is the increment of the quantity x_i in time $\delta\tau$, occurring due to the laws of dynamics in a closed system of n particles. Subdividing the time τ into time intervals $\delta\tau$ we find

$$e^{\tau\hat{L}_n}\psi(x_1,\ \ldots,\ x_n,\ t)$$

$$=\lim_{\delta\tau\to 0}(1+\delta\tau\hat{L}_n)^{\tau/\delta\tau}\psi(x_1,\ \ldots,\ x_n,\ t)=\psi(X_1,\ \ldots,\ X_n,\ t).$$

Thus, if there exists some function of the dynamic variables of a closed system of n particles, $\psi(x_1,\ \ldots,\ x_n,\ t)$, then

$$\hat{S}_n(\tau)\,\psi(x_1,\ \ldots,\ x_n,\ t)=\psi[\hat{S}_n(\tau)\,x_1,\ \ldots,\ \hat{S}_n(\tau)\,x_n,\ t]$$

$$=\psi(X_1,\ \ldots,\ X_n,\ t),\qquad(87.12)$$

where X_i is the totality of the quantities R_i, V_i—coordinates and velocities that the particles of the system would have in time τ if the system of n particles were closed. The quantities X_i, except t, evidently, depend on all x_i.

Thus, the operators $S_n(\tau)$ describe the evolution in time of any functions of the coordinates and velocities of a closed system. It is clear that they possess the following properties:

$$\hat{S}_n(\tau_1)\,\hat{S}_n(\tau_2)=\hat{S}_n(\tau_1+\tau_2),\quad \hat{S}_n(\tau)\,\hat{S}_n(-\tau)=\hat{S}_n(0)=1.$$

Let us return now to Eq. (87.7) and note that since the functional $F_2^{(0)}(x_1,\ x_2|\ F_1(y,\ t))$ does not depend on the argument y of function $F_1(y,\ t)$, we can replace in this equation $F_1(y,\ t)$ by $S_1(\tau)\,F_1(y,\ t)=F_1(Y,\ t)$.

Then, let us make use of relationship

$$\frac{d}{d\tau}[\hat{S}_1(\tau)\,F_1(x,\ t)]=\frac{d}{d\tau}[e^{\tau\hat{L}_1}F_1(x,\ t)]=\hat{L}_1\hat{S}_1(\tau)\,F_1(x,t)\quad(87.13)$$

and replace the factor $\hat{L}_1\hat{S}_1(\tau)F_1(y, t)$ in (87.10) with the aid of formula (87.13):

$$\frac{\partial F_2^{(0)}}{\partial t} = -\int A(x_1, x_2, y)\,\Phi'[\hat{S}(\tau)F_1]\frac{d}{d\tau}[\hat{S}_1(\tau)F_1]\,dy = -\frac{\partial F_2^{(0)}}{\partial \tau}$$

Equation (87.7) now reduces to

$$\frac{d}{d\tau}F_2^{(0)}[x_1, x_2 \mid \hat{S}_1(\tau)F_1] = \hat{L}_2 F_2^{(0)}[x_1, x_2 \mid \hat{S}_1(\tau)F_1], \quad (87.14)$$

and its formal solution can be written at once with the aid of the operator $\hat{S}_2(\tau)$:

$$F_2^{(0)}[x_1, x_2 \mid \hat{S}_1(\tau)F_1] = e^{\tau\hat{L}_2}F_2^{(0)}(x_1, x_2 \mid F_1)$$
$$= \hat{S}_2(\tau)F_2^{(0)}(x_1, x_2 \mid F_1). \quad (87.15)$$

To find the integration "constant" $F_2^{(0)}(x_1, x_2 \mid F_1)$, the initial condition for $F_2^{(0)}(x_1, x_2 \mid \hat{S}_1(\tau)F_1)$ must be given as a function of τ. According to Bogoliubov, this initial condition is chosen in the following way. If we ignore the possibility of the molecules "sticking together" and forming more intricate complexes, i.e. assume the potential $u(r_{ik})$ to be monotonically decreasing with increasing r_{ik} and practically equal to zero at $r_{ik} > r_0$, then in a closed system of two particles the condition

$$\lim_{\tau\to\infty}\hat{S}_2(\pm\tau)\,|\mathbf{r}_1 - \mathbf{r}_2| = \infty \quad (87.16)$$

is satisfied. According to this condition, whatever the mutual distance $\mathbf{r}_{12}$ between two particles at the given instant of time, in the infinite past and in the infinite future they will be arranged at a considerable distance from one another and will in no case interact. It is, therefore, natural to assume that as $\tau \to \pm\infty$ the states of the two particles are statistically independent of each other. This permits us to impose on $F_2^{(0)}(x_1, x_2, t)$ an initial condition of one of the two types:

$$\lim_{\tau\to\infty}\hat{S}_2(-\tau)\,[F_2^{(0)}(x_1, x_2, t) - F_1(x_1, t)F_1(x_2, t)] = 0, \quad (87.17)$$

or

$$\lim_{\tau\to\infty}\hat{S}_2(\tau)\,[F_2^{(0)}(x_1, x_2, t) - F_1(x_1, t)F_1(x_2, t)] = 0.$$

It should be noted that these conditions are not of a dynamic nature and represent purely statistical, probability postulates. It turns out that the first condition (87.17) leads to a correct kinetic equation, ensuring the required irreversibility of a macroscopic process—increase in entropy with time. This condition, referred to as the *correlation weakening condition*, will be used below. The second condition leads to a kinetic equation with a changed sign of

the collision integral, which would mean a wrong irreversibility, namely, a decrease of entropy with time.

It should be noted that the function $F_2^{(0)}(x_1, x_2 \mid F_1)$ depends in a functional way on $F_1(y, t)$ and the condition (87.17) must be satisfied at any selection of the arguments y, t. We can, therefore, replace $F_1(y, t)$ by $\hat{S}_1(\tau) F_1(y, t)$ and finally present the initial condition for Eq. (87.14) in the form

$$\lim_{\tau \to \infty} \hat{S}_2(-\tau) [F_2^{(0)}(x_1, x_2 \mid \hat{S}_1(\tau) F_1(y, t)) - \hat{S}_1(\tau) F_1(x_1, t) F_1(x_2, t)] = 0. \quad (87.18)$$

Acting on both sides of Eq. (87.15) with the operator $\hat{S}_2(-\tau)$, we find

$$F_2^{(0)}(x_1, x_2 \mid F_1) = \hat{S}_2(-\tau) F_2^{(0)}(x_1, x_2 \mid \hat{S}_1(\tau) F_1).$$

Since the left-hand side of this equation does not contain τ, it is valid at any τ. Passing to the limit $\tau \to \infty$ and using Eq. (87.18), we find

$$F_2^{(0)}(x_1, x_2 \mid F_1) = \lim_{\tau \to \infty} \hat{S}_2(-\tau) \hat{S}_1(\tau) F_1(x_1, t) F_1(x_2, t). \quad (87.19)$$

Thus, to terms of the order of r_0^3/ω, kinetic equation (87.6) reduces to

$$\frac{\partial F_1(x_1, t)}{\partial t} + \hat{L}_1 F_1(x_1, t) = -\frac{1}{\omega} \int \mathbf{w}_{12} \frac{\partial}{\partial \mathbf{v}_1} [F_1(X_1, t) F_1(X_2, t)] dx_2, \quad (87.20)$$

where

$$X_i = \lim_{\tau \to \infty} \hat{S}_2(-\tau) \hat{S}_1(\tau) x_i.$$

Before passing to a more detailed consideration of Eq. (87.20), it will be shown that the above method also permits finding the next terms in the kinetic equation, i.e. the terms of the second, third, etc. order in r_0^3/ω.

In fact, to find in the kinetic equation (87.6) terms, for instance, of the second order in r_0^3/ω, we must find the functional dependence of $F_2^{(0)}$ on F_1. This can be done by using the equation for the function $F_2^{(0)}$ stemming from Eq. (86.12), turning it into a differential equation just as it was done with Eq. (87.7). The function $F_3^{(0)}$ on the right-hand side of Eq. (87.7) can be found from the equation

$$\frac{\partial F^{(0)}}{\partial t} + \hat{L}_3 F_3^{(0)} = 0,$$

assuming for the initial condition

$$\lim_{\tau \to \infty} \hat{S}_3(-\tau) [F_3^{(0)}(x_1, x_2, x_3, t) - F_1(x_1, t) F_1(x_2, t) F_1(x_3, t)] = 0.$$

Thus, it becomes possible to find the kinetic equation with account taken of terms of the $(k-1)$th order in r_0^3/ω, where k is an integral, i.e. with account taken of k-particle collisions.

Let us return now to Eq. (87.20) and show that in the special case of a spatially uniform system, when F_1 is independent of coordinates $\mathbf{r}_1$, this equation coincides with the Boltzmann kinetic (transport) equation. It should be noted in the first place that in the case of a spatially homogeneous system

$$F_1 = F_1(\mathbf{v}_1, t), \quad \hat{L}_1 F_1 = \mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1}(F_1) = 0.$$

Further the operator $\hat{S}_1(\tau)$ for spatially homogeneous functions becomes an identity transformation operator and can be omitted. Equation (87.20) reduces to

$$\frac{\partial F_1(\mathbf{v}_1, t)}{\partial t} = -\frac{1}{\omega}\int \mathbf{w}_{12}\frac{\partial}{\partial \mathbf{v}_1}[F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)]\, d^3r_2\, d^3v_2, \quad (87.21)$$

where

$$\mathbf{V}_i = \lim_{\tau\to\infty} \hat{S}_2(-\tau)\mathbf{v}_i.$$

The integrand in Eq. (87.21) can be further transformed in the following manner. The quantities $\mathbf{V}_i$ represent, at $t \to -\infty$, the limit values of the velocities of particles having at $t = 0$ velocities $\mathbf{v}_i$, spaced by $\mathbf{r}_{12}$ and forming a closed system. Consequently, the quantities $\mathbf{V}_i$ are independent of time, and the functions $F_1(\mathbf{V}_i, t)$ depend on time only through the argument t. This means that the total derivative of the function $F_1(\mathbf{V}_i, t)$ with respect to time coincides with the partial derivative. On the other hand, due to the dynamic equations of motion, $\mathbf{V}_1$ and $\mathbf{V}_2$ are single-valued functions of the initial conditions, i.e. of the quantites $\mathbf{v}_1$, $\mathbf{v}_2$ and $\mathbf{r}_{12}$. With this in mind, assuming the arguments $\mathbf{V}_1$ and $\mathbf{V}_2$ to be expressed in terms of $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{r}_{12}$, the difference between the total and partial derivatives of the product $F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)$ with respect to time is represented by the expression

$$\left[\frac{d\mathbf{v}_1}{dt}\frac{\partial}{\partial \mathbf{v}_1} + \frac{d\mathbf{v}_2}{dt}\frac{\partial}{\partial \mathbf{v}_2} + \frac{d\mathbf{r}_{12}}{dt}\frac{\partial}{\partial \mathbf{r}_{12}}\right] F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)$$
$$= \left[\mathbf{w}_{12}\frac{\partial}{\partial \mathbf{v}_1} + \mathbf{w}_{21}\frac{\partial}{\partial \mathbf{v}_2} + \mathbf{q}\frac{\partial}{\partial \mathbf{r}_{12}}\right] F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t) = 0,$$

where $\mathbf{q} = \mathbf{v}_2 - \mathbf{v}_1$ is the relative velocity of particles.

Thus, we can replace the integrand in Eq. (87.21) by the expression

$$-\left[\mathbf{q}\frac{\partial}{\partial \mathbf{r}_{12}} + \mathbf{w}_{12}\frac{\partial}{\partial \mathbf{v}_2}\right] F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t).$$

In this case, due to the Gauss theorem, the integral of the second term vanishes as the integral of divergence in the velocity space, and we obtain

$$\frac{\partial F_1(\mathbf{v}_1, t)}{\partial t} = \frac{1}{\omega}\int \mathbf{q}\frac{\partial}{\partial \mathbf{r}_{12}}[F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)]\, d^3r_{12}\, d^3v_2. \quad (87.22)$$

Here we passed from integration over d^3r_2 to integration over d^3r_{12}. The Jacobian of this transformation is equal to unity.

Let us integrate in Eq. (87.22) over d^3r_{12}, passing to the cylindrical coordinates with the axis directed along the relative velocity. Denoting the coordinate along this axis by ζ, the coordinate along the axis perpendicular to the latter by ρ and the polar angle by φ, we obtain

$$\int \mathbf{q} \frac{\partial}{\partial \mathbf{r}_{12}} [F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)] d^3r_{12}$$

$$= \int\int \mathbf{q}\rho \, d\rho \, d\varphi \int_{-\infty}^{\infty} \frac{\partial}{\partial \zeta} [F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)] d\zeta$$

$$= \int\int \mathbf{q} [F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)|_{\zeta=\infty} - F_1(\mathbf{V}_1, t) F_1(\mathbf{V}_2, t)|_{\zeta=-\infty}] \rho \, d\rho \, d\varphi. \quad (87.23)$$

It should be noted now that as $\zeta \to -\infty$ the distance between the particles 1 and 2 is considerably greater than r_0 and they do not interact with each other. The action of the operator $\hat{S}_2(-\tau)$, i.e. a shift into the past by time $-\tau$, does not result in the particles' collision, since the direction of the relative velocity $\mathbf{q}$ is chosen along the ζ-axis; with a shift into the past the relative motion of particles 1 and 2 leads to an increase in the absolute value of ζ. It follows that as $\zeta \to -\infty$ the limit values of $\mathbf{V}_1$ and $\mathbf{V}_2$ must be identified with the velocities of the particles 1 and 2 "before collision", $\mathbf{v}_1$ and $\mathbf{v}_2$. As $\zeta \to \infty$ the molecules 1 and 2 do not interact with each other as well. But the shift into the past by a sufficiently large time τ due to the action of the operator $S_2(-\tau)$ will lead to a molecular collision without fail, since with a shift into the past the relative motion of the particles diminishes the absolute value of ζ. Therefore, as $\zeta \to \infty$, the limit values of $\mathbf{V}_1$ and $\mathbf{V}_2$ must be identified with the velocities of molecules 1 and 2 "after collision", $\tilde{\mathbf{v}}_1$, $\tilde{\mathbf{v}}_2$. It should also be noted that the velocities "after collision", $\tilde{\mathbf{v}}_1$ and $\tilde{\mathbf{v}}_2$, are the functions of velocities "before collision", $\mathbf{v}_1$ and $\mathbf{v}_2$, and of the impact parameter ρ. The integration over ρ in Eq. (87.23) is practically limited by the quantity of the order of r_0, since at $\rho > r_1$ no "impact" actually takes place, the particles failed to interact and the difference $F_1(\tilde{\mathbf{v}}_1, t) F_1(\tilde{\mathbf{v}}_2, t) - F_1(\mathbf{v}_1, t) F_1(\mathbf{v}_2, t)$ vanishes, so that the integral over ρ converges.

In order to compare the kinetic equation derived in this section with Boltzmann's equation presented in the form (85.23), account must be taken of the fact that the function $F_1(\mathbf{r}, \mathbf{v}, t)$ and the function $f(\mathbf{r}, \mathbf{v}, t)$, pertinent in Eq. (85.23), obey different normaliza-

tion conditions: for the function $F_1(\mathbf{r}, \mathbf{v}, t)$ we have

$$\int F_1(\mathbf{r}, \mathbf{v}, t)\, d^3r\, d^3v = V,$$

while for the function $f(\mathbf{r}, \mathbf{v}, t)$ it is

$$\int f(\mathbf{r}, \mathbf{v}, t)\, d^3r\, d^3v = N,$$

whence it follows that $F_1 = fV/N = f\omega$.

Taking into account the foregoing, we obtain in the spatially homogeneous case for function $f(\mathbf{r}, \mathbf{v}, t)$ the kinetic equation

$$\frac{\partial f}{\partial t}(\mathbf{v}_1, t) = \int d^3v_2 \int\int q\,[f(\tilde{\mathbf{v}}_1, t)\, f(\tilde{\mathbf{v}}_2, t) - f(\mathbf{v}_1, t)\, f(\mathbf{v}_2, t)]\, \rho\, d\rho\, d\varphi. \quad (87.24)$$

In Eq. (87.24) we can pass from the integration over the impact parameter ρ and angle φ to the integration with respect to the directions of the unit vector $\mathbf{e}$ collinear to the change of velocity $\tilde{\mathbf{v}}_1 - \mathbf{v}_1$ by using the fact for the given values of $\mathbf{v}_1$, $\mathbf{v}_2$ and ρ there corresponds a direction of vector $\mathbf{e}$ unambiguously determined by dynamics of impact. Since

$$\rho\, d\rho\, d\varphi = d\sigma(q, \theta)$$

(θ is the scattering angle, $\theta = \widehat{\mathbf{v}_1, \tilde{\mathbf{v}}_1}$), we obtain from Eq. (87.24) the equation

$$\frac{\partial f(\mathbf{v}_1, t)}{\partial t} = \int\int d^3v_2 q\, d\sigma\, (\tilde{f}_1 \tilde{f}_2 - f_1 f_2)$$

for a spatially homogeneous system in the absence of an applied field, which precisely coincides with Boltzmann's equation.

If we discard the condition of spatial homogeneity and assume that the function f depends also on coordinates, the appearing equation was shown by Bogoliubov to differ somewhat from Boltzmann's equation.

Problems

1. Find the result of the action of the operator $\hat{S}_2(\tau)$ on $\mathbf{r}_i$ and $\mathbf{v}_i$ to the third-order terms in τ^3 for $\hat{S}_2(\tau)\, \mathbf{r}_i$ and to the second-order terms in τ for $\hat{S}_2(\tau)\, \mathbf{v}_i$.
2. Verify with the aid of the operator $\hat{S}_2(\tau)$ the theorem about the motion of the centre of inertia for an isolated system of two particles.

§88. Dimensionless Form of Bogoliubov's Equations. Factorization and the Correlation Functions. Free-Molecule Flow

This and the following section will be devoted to some methods of approximate integration of Bogoliubov's system of equations. These methods are based on the fact that in two cases of a considerably rarefied gas and weak interaction between gas particles, the effect of one particle on the state of other particles must become weak, and a tentative assumption can be made that in a zeroth approximation the n-particle distribution function is factorized, i.e. can be represented as the product of one-particle functions:

$$F_n^{(0)}(x_1, \ldots, x_n, t) = \prod_{i=1}^{n} F_1(x_i, t). \tag{88.1}$$

The deviation of an exact n-particle function from the factorized zeroth approximation is usually characterized by the so-called *correlation functions* $G_n(x_1, \ldots, x_n, t)$ which can be found in the following way.

For a two-particle function we have

$$F_2^{(0)}(x_1, x_2, t) = F_1(x_1, t) F_1(x_2, t), \tag{88.2}$$

$$F_2(x_1, x_2, t) = F_2^{(0)}(x_1, x_2, t) + G_2(x_1, x_2, t). \tag{88.3}$$

For a three-particle function,

$$F_3^{(0)}(x_1, x_2, x_3, t) = F_1(x_1, t) F_1(x_2, t) F_1(x_3, t). \tag{88.4}$$

$$\begin{aligned} F_3(x_1, x_2, x_3, t) = {} & F_3^{(0)}(x_1, x_2, x_3, t) + F_1(x_1, t) G_2(x_2, x_3, t) \\ & + F_1(x_2, t) G_2(x_3, x_1, t) + F_1(x_3, t) G_2(x_1, x_2, t) \\ & + G_3(x_1, x_2, x_3, t), \quad \text{etc.} \end{aligned} \tag{88.5}$$

Let us now formulate quantitatively the condition for gas rarefaction and the condition for weak interaction. Let r_0 denote the range of molecular interaction and $\mathcal{U}_0$ the characteristic value of the potential energy of interaction. The case of a rarefied gas is realized when r_0 is much less than the mean particles separation $\omega^{1/3}$ and, consequently, in this case the small parameter of the problem is the quantity $\alpha = r_0^3/\omega = n r_0^3$. The case of weak interaction is realized when the potential energy is small compared with the kinetic energy which is proportional to T. It follows that in this case the small parameter of the problem is the quantity $\beta = \mathcal{U}_0/T$.

We assume that in the two cases particles' coordinates and velocities are weakly correlated and the correlation functions $G_n(x_1, \ldots, x_n, t)$ are small with respect to parameters α or β respectively.

To derive the methods of solution for Bogoliubov's system of equations on these assumptions, we write the system (86.7) in a

more detailed form,

$$\frac{\partial F_n}{\partial t} + (\hat{K}_n + \hat{V}_n) F_n = \frac{N-n}{V} \hat{A}_n F_{n+1}, \tag{88.6}$$

singling out in the operator $\hat{L}_n = \hat{K}_n + \hat{V}_n$ the terms including and not containing the interaction potential:

$$\hat{K}_n = \sum_{i=1}^{n} \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i}, \tag{88.7}$$

$$\hat{V}_n = \sum_{i=1}^{n} \mathbf{w}_{ik} \frac{\partial}{\partial \mathbf{v}_i}, \tag{88.8}$$

$$\hat{A}_n = -\sum_{i=1}^{n} \int dx_{n+1} \mathbf{w}_{i,\, n+1} \frac{\partial}{\partial \mathbf{v}_i}. \tag{88.9}$$

Let us pass in Eqs. (88.6) to dimensionless variables, choosing as the unit of length r_0, unit of velocity $\sqrt{T/m}$, unit of acceleration $\mathcal{U}_0/mr_0$ and unit of time $r_0\sqrt{m/T}$. For the sake of simplicity we do not introduce new notations for the dimensionless variables and make the substitutions in Eqs. (88.6):

$$\begin{aligned} &\mathbf{r}_i \to \mathbf{r}_i r_0, && \mathbf{v}_i \to \mathbf{v}_i \sqrt{\frac{T}{m}}, \\ &\mathbf{w}_{ik} \to \mathbf{w}_{ik} \frac{\mathcal{U}_0}{mr_0}, && t \to t r_0 \sqrt{\frac{m}{T}}. \end{aligned} \tag{88.10}$$

In addition, allowing for the normalization condition (86.5) for the functions $F_n(x_1, \ldots, x_n, t)$, from which it follows that the dimensionality of F_n is $v^{-3n} = (m/T)^{3n/2}$, we introduce a new dimensionless distribution function by replacing

$$F_n \to F_n \left(\frac{m}{T}\right)^{3n/2}. \tag{88.11}$$

Then, for $n \ll N$ Bogoliubov's equations (88.6) take the form

$$\frac{\partial F_n}{\partial t} + (\hat{K}_n + \beta \hat{V}_n) F_n = \alpha\beta \hat{A}_n F_{n+1}. \tag{88.12}$$

It should be noted that assuming the factorization of the functions F_n in a zeroth approximation, $F_n^{(0)} = F_1(x_1, t) F_1(x_2, t) \ldots F_1(x_n, t)$ we obtain N equations for the same function $F_1(x_i, t)$. It is clear that the necessary condition for the factorization is the compatibility of these equations in a zeroth approximation.

Let us make sure that the case of a rarefied gas ($\alpha = r_0^3/\omega \ll 1$, $\beta = \mathcal{U}_0/T \gg 1$ leads in a zeroth approximation to a non-self-consistent system. In fact, in a zeroth approximation the system of equa

tions (88.12) takes the following form:

$$\frac{\partial F_1^{(0)}}{\partial t} + \hat{K}_1 F_1^{(0)} = 0,$$

$$\left(\frac{\partial}{\partial t} + \hat{K}_2\right) F_1^{(0)}(x_1, t) F_1^{(0)}(x_2, t) + \beta \hat{V}_2 F_1^{(0)}(x_1, t) F_1^{(0)}(x_2, t) = 0,$$

. . . . . .

It is readily seen that the equations of this system are compatible only if there is no interaction between particles, i.e. $w_{ik} = 0$. Consequently, in the case of a rarefied gas, correlations must not be ignored even in a zeroth approximation. Strictly speaking, this was to be expected, since for a rarefied gas with $\alpha \ll 1$ a "good" kinetic equation is the Boltzmann equation which is incompatible with the factorization requirement. It was shown above that Bogoliubov's derivation of the Boltzmann equation presupposes only the factorisation of the function F_s in the "infinite past".

Let us consider the case of $\beta = \mathcal{U}_0/T \ll 1$, $\alpha = r_0^3/\omega \lesssim 1$, corresponding to a hot gas with a weak interaction between particles, which may, however, be sufficiently dense. Actually, with a potential well of a typical depth, $\mathcal{U}_0 \sim (10^{-1}\text{-}10^{-2})$ eV, the condition $\mathcal{U}_0/T \ll 1$ is already satisfied at room temperature. Then in a zeroth approximation this yields separable equations:

$$\frac{\partial F_n^{(0)}}{\partial t} = \hat{K}_n F_n^{(0)} = 0, \tag{88.13}$$

in which the variables $x_1, \ldots, x_n$ are separable. This means that the assumption that $F_n^{(0)}(x_1, \ldots, x_n, t) = \prod_{i=1}^{n} F_n^{(0)}(x_i, t)$ is self-consistent and the one-particle function $F_1^{(0)}(\mathbf{r}, \mathbf{v}, t)$ satisfies the equation

$$\frac{\partial F_1^{(0)}}{\partial t} + \mathbf{v} \frac{\partial F_1^{(0)}}{\partial \mathbf{r}} = 0. \tag{88.14}$$

Integrating the equation of characteristics

$$\frac{dt}{1} = \frac{dx}{v_x} = \frac{dy}{v_y} = \frac{dz}{v_z}, \tag{88.15}$$

we find the solution of Eq. (88.14) in the form

$$F_1^{(0)}(\mathbf{r}, \mathbf{v}, t) = \psi(\mathbf{r} - \mathbf{v}t, \mathbf{v}), \tag{88.16}$$

where $\psi(\mathbf{r}, \mathbf{v}, t)$ is an arbitrary function of its arguments, compatible with the initial and boundary conditions. It follows from (88.16) that $F_1^{(0)}(\mathbf{r}, \mathbf{v}, t)$ remains constant along the dynamic trajectory of particles in the μ-space, which was to be expected for a system of weakly interacting particles in a zeroth approximation.

The following approximations for the functions F_n can be found successively from the equations

$$\left(\frac{\partial}{\partial t}+\hat{K}_1\right)F_1=\alpha\beta\hat{A}_1F_1(x_1,\ t)\,F_1\ (x_2,\ t),$$

$$\left(\frac{\partial}{\partial t_1}+\hat{K}_2\right)[F_1(x_1,\ t)\,F_1(x_2,\ t)+G_2(x_1,\ x_2,\ t)] \tag{88.17}$$

$$+\beta\hat{V}_2F_1(x_1,\ t)\,F_1(x_2,\ t)=\alpha\ \hat{A}_2F_1(x_1,\ t)\,F_1(x_2,\ t)\,F_1(x_3,\ t),$$

. . . . . .

Solving the first of these equations, one can find in principle F_1, then solving the second equation, find G_2 and, consequently, F_2, etc.

We shall limit ourselves to the zeroth approximation (88.16) and examine by way of illustration the problem of free expansion of a gas into a vacuum, following the treatment given in [40]. Let at the initial instant of time $t = 0$ a gas with a Maxwellian velocity distribution be confined in a one-dimensional case within a half space $x < 0$. The wall $x = 0$ is then removed, and the gas begins to expand.

The initial distribution f (r, v, 0) is given by the formula

$$f(x,\ \mathbf{v},\ 0)=n\left(\frac{m}{2\pi T}\right)^{3/2}e^{-mv^2/2T}\sigma(-x), \tag{88.18}$$

where $\sigma(x)$ is a step function [it should be recalled that the function f (r, v, t) is connected with F_1 (r, v, t) by the relationship $f = F_1 n = F_1/\omega$].

According to (88.16), the time development of the function f (x, v, 0) is given by the formula

$$f(x,\ \mathbf{v},\ t)=n\left(\frac{m}{2\pi T}\right)^{3/2}e^{-mv^2/2T}\sigma(-x+v_xt). \tag{88.19}$$

The spatial particles' density at point x at the instant of time t is equal to

$$n(x,\ t)=\int d^3v f(x,\ \mathbf{v},\ t)=n\left(\frac{m}{2\pi T}\right)^{1/2}\int_{x/t}^{\infty}e^{-mv_x^2/2T}\,dv_x$$

$$=\frac{n}{2}\left[1-\operatorname{erf}\left(\frac{x}{t}\sqrt{\frac{m}{2T}}\right)\right], \tag{88.20}$$

and the mean velocity of the gas u (x, t) is equal to

$$u(x,\ t)=\frac{1}{n(x,\ t)}\int d^3v v_x f(x,\ \mathbf{v},\ t)$$

$$=\frac{n}{n(x,\ t)}\left(\frac{m}{2\pi T}\right)^{1/2}\int_{x/t}^{\infty}dv_x\,v_xe^{-mv_x^2/2T}$$

$$=\frac{n}{n(x,\ t)}\sqrt{\frac{T}{2\pi m}}\,e^{-mx^2/2T^2}. \tag{88.21}$$

Since $n(x, t)$ and $u(x, t)$ depend only on x/t, both the spatial gas density distribution and spatial velocity distribution remain similar and the locus of equal densities and equal velocities of flow moves uniformly along the x-axis.

The following observation should be made in concluding this section. Since the equation of a free-molecule flow (88.14) is a Liouville's single-particle equation, it represents a mechanical and not a statistical statement, and the statistical meaning is "forced" into it. This manifests itself, in particular, in the invertible solutions of Eq. (88.14). If, for instance, at $t = t_0$ the solution of (88.19) is assumed to be the initial condition and is continued in time by replacing x by $x + v_x t$, which reverses the direction of velocities of all particles, then, after a time interval t_0 we shall come to the initial state, Eq. (88.18). In the motion reversed in this way the gas is spontaneously compressed instead of undergoing expansion, and irreversibility is absent.

Problems

1. In the above problem study the behaviour of $n(x, t)$ and $u(x, t)$ as $|x|/t \to \infty$ and $x/t \to 0$ ($x > 0$ and $x < 0$).
2. Consider the layer of a gas placed at the initial instant of time between the planes $x = -\mathscr{L}$ and $x = \mathscr{L}$ and find the subsequent change in $n(x, t)$ and $u(x, t)$.

§90. Equation of a Self-Consistent Field. Collisionless Plasma

Let us investigate Eqs. (88.12) in the case of sufficiently high temperatures, so that the parameter β is small, $\beta = \mathcal{U}_0/T \ll 1$ but the interaction forces are long-range, and $\alpha = r_0^3/\omega \gg 1$. The product $\alpha\beta = \mathcal{U}_0 r_0^3/\omega T$ is also assumed to be of the order of unity. This case is of considerable practical importance, since it permits a description of the behaviour of a high-temperature plasma in which the collisions of particles can be ignored, but the long-range nature of Coulomb's interaction forces should, however, be taken into account. It is readily seen that the parameter r_0 acquires then the meaning of Debye's screening radius. In fact, assuming $\mathcal{U}_0 \sim e^2/r_0$ and equating $\alpha\beta$ to unity, $\alpha\beta = e^2 r_0^2 n/T \approx 1$, we obtain $r_0 \sim \sqrt{T/ne^2} \sim r_D$.

Let us use the intuitively plausible although not rigorously proved assumption (for greater detail see [41]) that the order of smallness of the correlation functions $G_n(x_1, \ldots, x_n, t)$ in parameter $\beta \ll 1$ is the higher the greater n. Then, in the zeroth order in β Bogoliubov's equations (88.12) can be presented in the form

$$\left(\frac{\partial}{\partial t}+\hat{K}_1\right) F_1(x_1,\ t)=\alpha\beta\hat{A}_1F_1(x_1,\ t)\,F_1(x_2,\ t),$$

$$\left(\frac{\partial}{\partial t}+\hat{K}_2\right) F_1(x_1,\ t)\,F_1(x_2,\ t)=\alpha\beta\hat{A}_2F_1(x_1,\ t)\,F_1(x_2,\ t)\,F_1(x_3,\ t), \tag{89.1}$$

. . . . . .

$$\left(\frac{\partial}{\partial t}+\hat{K}_n\right)\prod_{i=1}^{n}F_1(x_i,\ t)=\alpha\beta\hat{A}_n\prod_{i=1}^{n+1}F_1(x_i,\ t).$$

It is readily seen that due to the additivity of the operators $\hat{K}_n$ and $\hat{A}_n$, the system of equations (89.1) is self-consistent: the separation of variables in any equation of this system yields the same equation for the function F_1, namely, to the first equation, and, on the contrary, the function F_1 satisfying the first equation of system (89.1) satisfies automatically any equation of this system.

Thus, returning again to the dimensionless variables and passing to the functions $f(\mathbf{r}, \mathbf{v}, t)$, we come to the equation

$$\frac{\partial f(x_1,\ t)}{\partial t}+\mathbf{v}_1\frac{\partial f(x_1,\ t)}{\partial \mathbf{r}_1}+\frac{\partial}{\partial \mathbf{v}_1}\int dx_2\mathbf{w}_{12}f(x_1,\ t)\,f(x_2,\ t)=0. \tag{89.2}$$

Equation (89.2) can be written in a somewhat different form by introducing $\overline{\mathcal{F}}(\mathbf{r}_1)$—the force of interaction between particles 1 and 2, averaged over the positions of the second particle:

$$\overline{\mathcal{F}}(\mathbf{r}_1)=m\int d^3r_2\mathbf{w}_{12}n(\mathbf{r}_2)=m\int\int d^3r_2\,d^3v_2\mathbf{w}_{12}f(x_2,\ t). \tag{89.3}$$

Equation (89.2) now reduces to

$$\frac{\partial f(x_1,\ t)}{\partial t}+\mathbf{v}_1\frac{\partial f(x_1,\ t)}{\partial \mathbf{r}_1}+\overline{\mathcal{F}}(\mathbf{r}_1)\frac{\partial f(x_1,\ t)}{\partial \mathbf{p}_1}=0. \tag{89.4}$$

This equation coincides in form with the Liouville's one-particle equation for a particle set in motion by a preset external force $\overline{\mathcal{F}}(\mathbf{r}_1)$, or, which is the same, with Boltzmann's equation without the term due to collision. The principal difference consists, however, in that in Eq. (89.4) the "external force" $\overline{\mathcal{F}}(\mathbf{r}_1)$ is not given and it is a functional of $f(\mathbf{r},\ \mathbf{v},\ t)$ specified by Eq. (89.3). Therefore Eq. (89.4), *named after A.A. Vlasov*, describes the self-consistent motion of a particle in the μ-space. The self-consistency of the solutions of the Vlasov equation must manifest itself in the following: if $\overline{\mathcal{F}}(\mathbf{r}_1)$ is given arbitrarily and Eq. (89.4) is solved, the function $f(\mathbf{r}, \mathbf{v}, t)$ must lead in formula (89.3) to the same value of $\overline{\mathcal{F}}(\mathbf{r}_1)$. On the contrary, if a definite function $f(\mathbf{r},\ \mathbf{v},\ t)$ is given and the force $\overline{\mathcal{F}}(\mathbf{r}_1)$ is found by formula (89.3), then by solving Eq. (89.4) we must get the initial function $f(\mathbf{r}, \mathbf{v}, t)$.

Problems

1. Show that in the equilibrium state the equation of a self-consistent field can be reduced to the form

$$\mathcal{U}(\mathbf{r}_1) = \lambda \int u(|\mathbf{r}_1 - \mathbf{r}_2|)\, e^{-\mathcal{U}(\mathbf{r}_1)/T}\, d^3r_2, \quad \lambda = \frac{N}{\int e^{-\mathcal{U}(\mathbf{r})/T}\, d^3r},$$

where $\mathcal{U}(\mathbf{r}_1)$ is a two-particle interaction potential $u(|\mathbf{r}_1 - \mathbf{r}_2|)$ averaged over the positions of the second particle:

$$\mathcal{U}(\mathbf{r}_1) = \int u(|\mathbf{r}_1 - \mathbf{r}_2|)\, f(x_2)\, dx_2 = \int u(|\mathbf{r}_1 - \mathbf{r}_2|)\, n(\mathbf{r}_2)\, d^3r_2.$$

2. Find a spatially homogeneous solution $\mathcal{U}(r) = \mathcal{U}_0 = \text{const}$, $n(r) = N/V$.

Answer. $\mathcal{U}_0 = \frac{N}{V} \int u(\rho)\, d^3\rho$.

3. Introducing $\varphi(\mathbf{r}) = \mathcal{U}(\mathbf{r}) - \mathcal{U}_0$, obtain the equation

$$\varphi(\mathbf{r}_1) = \lambda' \int u(|\mathbf{r}_1 - \mathbf{r}_2|)\, (e^{-\varphi(\mathbf{r}_2)/T} - 1)\, d^3r_2, \quad \lambda' = \lambda e^{-\mathcal{U}_0/T}$$

and find the condition on which the equation has periodic solutions of the form $\varphi = e^{i\mathbf{kr}}$ correct to the first-order infinitesimals $|\varphi|/T \ll 1$. Examine the result, including the limit as $k \to 0$.

Answer. The origination of a crystalline structure with a period (wavelength) of $2\pi/k$ is possible on condition that

$$\frac{4\pi N}{TV} \int_0^\infty u(\rho) \int_0^\infty \frac{\sin k\rho}{k\rho} \rho^2\, d\rho = -1, \tag{89.5}$$

which determines the period of the structure as a function of T. The maximum temperature at which crystallization is possible is determined by the condition $k \to 0$ ($\lambda \to \infty$) and is equal to $T_0 = -\frac{4\pi N}{V} \int_0^\infty u(\rho)\rho^2\, d\rho$. The condition for possible crystallization is that the integral in Eq. (89.5) must be negative, i.e. the attractive forces between particles must prevail over the repulsive forces.

90*. Oscillations of Electron Plasma

The application of Eq. (89.4) will be illustrated by examining the problem on oscillations of an electron plasma in the absence of an external field, first solved by L.D. Landau in his work [42]. These

oscillations originate due to local violations of plasma neutrality as a result of random motion of particles; in this case, due to the fact that the ionic masses are rather large compared with the mass of an electron, in a zeroth approximation only the motion of electrons can be taken into account.

In addition, the magnetic field is ignored, since the relative role of the magnetic effects is of the order of v/c, and a purely electrostatic field will be considered. Then, Eq. (89.4) takes the form

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \frac{e}{m}\frac{\partial \varphi}{\partial \mathbf{r}}\frac{\partial f}{\partial \mathbf{v}} = 0, \tag{90.1}$$

and the role of the equation that makes the system "consistent" will be played by the Poisson equation

$$\nabla^2\varphi = 4\pi e\int f\,d^3v. \tag{90.2}$$

We linearize Eq. (90.1) by representing the function f in the form

$$f = f_0(v) + F(\mathbf{r}, \mathbf{v}, t), \tag{90.3}$$

where $f_0(v)$ = equilibrium (Maxwellian) distribution function, $F(\mathbf{r}, \mathbf{v}, t)$ = small, compared with f_0, correction.

The equation for F has the form

$$\frac{\partial F}{\partial t} + \mathbf{v}\frac{\partial F}{\partial \mathbf{r}} + \frac{e}{m}\frac{\partial \varphi}{\partial \mathbf{r}}\frac{\partial f_0}{\partial \mathbf{v}} = 0, \tag{90.4}$$

and, accounting for the fact that the equilibrium charge $-e\int f_0\,d^3v$ is compensated for by a positive charge of the ions, Poisson's equation (90.2) can be written to read

$$\nabla^2\varphi = 4\pi e\int F\,d^3v. \tag{90.5}$$

Let there be given at the initial instant of time some non-equilibrium electron distribution, $F(\mathbf{r}, \mathbf{v}, 0)$. We are interested in the further evolution of the state. Due to the linearity of Eqs. (90.4) and (90.5), the function $F(\mathbf{r}, \mathbf{v}, t)$ can be expanded into a Fourier integral in exponentials $e^{i\mathbf{q}\mathbf{r}}$, meaning that it is sufficient to consider a solution of the form

$$F(\mathbf{r}, \mathbf{v}, t) = F(\mathbf{q}, \mathbf{v}, t)\,e^{i\mathbf{q}\mathbf{r}}, \quad \varphi(\mathbf{r}, t) = \varphi(\mathbf{q}, t)\,e^{i\mathbf{q}\mathbf{r}}$$

(the Fourier components of the functions F and φ are denoted by the same symbols). Equations (90.4) and (90.5) take the form (the x axis is directed along the vector $\mathbf{q}$)

$$\frac{\partial F}{\partial t} + iqv_xF + iq\frac{e}{m}\varphi\frac{\partial f_0}{\partial v_x} = 0, \tag{90.6}$$

$$q^2\varphi = 4\pi e\int F\,d^3v. \tag{90.7}$$

Landau solved the system of equations (90.6), (90.7) with the aid of the Laplace transform [42]. Let us introduce new functions

$$F_p(q, v) = \int_0^\infty F(q, v, t)\, e^{-pt}\, dt, \tag{90.8}$$

$$\varphi_p(q) = \int_0^\infty \varphi(q, t)\, e^{-pt}\, dt. \tag{90.9}$$

The inverse transformations (see Mathematical Appendix, XI) have the following form:

$$F(q, v, t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} F_p(q, v)\, e^{pt}\, dp, \tag{90.10}$$

$$\varphi(q, t) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \varphi_p(q)\, e^{pt}\, dp, \tag{90.11}$$

where $\sigma > 0$. We multiply both sides of Eqs. (90.6) and (90.7) by e^{-pt} and integrate over t. The first term in Eq. (90.6) is then transformed in the following way:

$$\int_0^\infty (\partial F/\partial t)\, e^{-pt}\, dt = Fe^{-pt}\Big|_0^\infty + p\int_0^\infty Fe^{-pt}\, dt = dF_p(q, v) - F(q, v, 0),$$

and the system of equations (90.6), (90.7) takes the form

$$(p + iqv_x) F_p + iq\frac{e}{m}\varphi_p \frac{\partial f_0}{\partial v_x} - F(q, v, 0) = 0, \tag{90.12}$$

$$q^2\varphi_p = 4\pi e \int F_p\, d^3v. \tag{90.13}$$

Equation (90.12) yields

$$F_p = \frac{F(q, v, 0) - iq\frac{e}{m}\varphi_p\frac{\partial f_0}{\partial v_x}}{p + iqv_x} \tag{90.14}$$

and, substituting this into Eq. (90.13), we obtain

$$\varphi_p = \frac{4\pi e}{q^2}\int \frac{F(q, v, 0)\, d^3v}{p + iqv_x}\left[1 + \frac{4\pi ie^2}{qm}\int \frac{\frac{\partial f_0}{\partial v_x}\, d^3v}{p + iqv_x}\right]^{-1}. \tag{90.15}$$

Integrating in Eq. (90.15) over v_y and v_z and introducing the notation $\int F(q, v, 0)\, dv_y\, dv_z = g(v_x)$, we find

$$\varphi_p = \frac{4\pi e}{q^2}\int_{-\infty}^{\infty} \frac{g(v_x)\, dv_x}{p + iqv_x}\left[1 + \frac{4\pi ie^2}{qm}\int_{-\infty}^{\infty}\frac{\partial f_0}{\partial v_x}\frac{dv_x}{p + iqv_x}\right]^{-1}, \tag{90.16}$$

where

$$f_0(v_x) = n\left(\frac{m}{2\pi T}\right)^{1/2} e^{-mv_x^2/2T} \qquad (90.17)$$

is Maxwell's one-dimensional distribution function.

Let us assume the initial distribution $g(v_x)$, given at real values of v_x, to be sufficiently "smooth", so that its analytical continuation into the region of complex values of v_x has no singularities at finite v_x, more exactly, that it is an integral function of the complex variable v_x. The same can, evidently, be said about the function $\partial f_0/\partial v_x$. So, the integrals in the numerator and the denominator of (90.16) are analytical functions of the complex variable p everywhere, except at the points on the imaginary axis Re $p = 0$. In the regions Re $p > 0$ and Re $p < 0$, however, each of these integrals determines two different analytical functions. Formulae (90.8) and (90.9) have a meaning only on condition Re $p > 0$.

As will be shown below, expression (90.16) must be investigated in the region Re $p < 0$ as well, for which purpose the corresponding integrals with Re $p > 0$ must be continued analytically into the region Re $p < 0$. To do this, still remaining with Re $p > 0$, we deform the integration contour over v_x, shifting it from the real axis into the lower half-plane, so as to bypass from below all essential for the problem poles $v_x = ip/q$, that can appear in the analytical continuation into the region Re $p < 0$. On condition Re $p > 0$ such a shift of the integration contour does not change the magnitude of the integrals, since we have not crossed the poles of the integrand, and at Re $p < 0$ we obtain an analytical continuation of Eq. (90.16) into this region. Thus, φ_p turns out to be the quotient of two integral functions in p, and the only singularities of this expression are the zeros of the denominator:

$$1 + \frac{4\pi e^2}{qm} \int_\Gamma \frac{(\partial f_0/\partial v_x)\, dv_x}{p + iqv_x} = 0 \qquad (90.18)$$

(Γ is the contour that passes below the essential poles $v_x = ip/q$).

Let p_0 be the root of Eq. (90.18) having the smallest real part by the absolute value (Re $p_0 < 0$). Then, in inversion formula (90.11) of the Laplace transform we can shift the integration contour from the straight line Re $p = \sigma$ so that it would bypass point p_0, and the other vertical segments would pass along the straight line Re $p = -A$, $A \gg$ Re p_0 (Fig. 110). Then, the integrals over the horizontal segments cancell out, at large time the integrals over the vertical segments are exponentially small ($\sim e^{-At}$), and the main contribution in the integral is made by the residue at the pole p_0. Thus, at large values of time the potential $\varphi(t)$ is proportional to $e^{p_0 t} = e^{t \operatorname{Re} p_0} e^{it \operatorname{Im} p_0}$, and the imaginary part of p_0 gives the frequency of the plasma wave ω_0, while its real part, the damping coefficient γ.

Let us solve Eq. (90.18) for the limiting case of long waves, $q \to 0$. Point $v_x = ip/q$ that must be bypassed in integrating in the v_x-plane [Fig. 111 (*a*)] gets into the region of very large $|v_x|$. Since in this region the function $\partial f_0/\partial v_x$ tends to zero, and the integrals

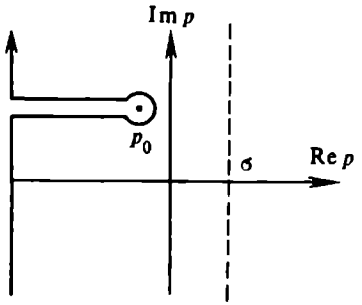


FIG. 110

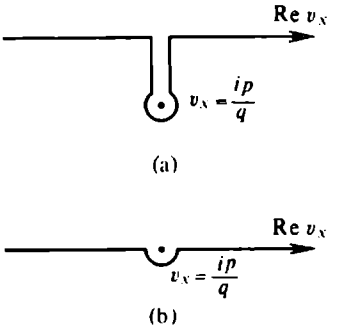


FIG. 111

over the vertical segments cancell out, the integration can actually be carried out along the real axis. Let us evaluate the integral in (90.18), expanding the integrand in powers of q. We obtain

$$\int_{-\infty}^{\infty} \frac{\partial f_0}{\partial v_x} \frac{dv_x}{p+iqv_x}$$

$$= -\frac{m}{Tp} \int_{-\infty}^{\infty} dv_x f_0 v_x \left[1 - \frac{iqv_x}{p} + \left(\frac{iqv_x}{p}\right)^2 - \left(\frac{iqv_x}{p}\right)^3 + \ldots\right].$$

In this expression all the integrals containing odd powers of v_x are equal to zero and the integrals containing even powers of v_x, according to formula (90.17), are expressed in terms of J_2, J_4, ... (Mathematical Appendix, IV). Equation (90.18) takes the form

$$1 + \frac{4\pi ne^2}{mp^2}\left(1 - \frac{3T}{m}\frac{q^2}{p^2}\right) = 0, \tag{90.19}$$

from which we find in a zeroth approximation

$$p_0 = i\sqrt{\frac{4\pi ne^2}{m}}. \tag{90.20}$$

It follows that longitudinal waves with a frequency $\omega_0 = \sqrt{4\pi ne^2/m}$ can propagate in plasma. In the next approximation, substituting in the small term $3Tq^2/mp^2$ the quantity p_0 for p, we obtain, accounting for $p = i\omega$,

$$\omega = \omega_0\left[1 + \frac{3T}{2m\omega_0^2}q^2\right] = \omega_0\left[1 + \frac{3}{2}q^2r_D^2\right], \tag{90.21}$$

where $r_D = \sqrt{T4\pi ne^2}$ is the Debye electron radius. The condition for the validity of the applied approximation is, evidently, the inequality $qr_D \ll 1$, i.e. the wavelength $2\pi/q$ must considerably exceed the Debye radius. In this approximation the second term in Eq. (90.21) is small, but essential, however, since it describes the dispersion of longitudinal oscillations and permits finding the group velocity of longitudinal plasma waves, $\frac{d\omega}{dq} = \frac{3Tq}{m\omega_0}$.

A more exact solution of Eq. (90.18) leads to the conclusion that there exists damping of longitudinal waves. Let us assume that as $q \to 0$, the real part of p_0 also tends to zero at a rate greater than q. This assumption will be confirmed by calculation below, and Re p_0 will be shown to decrease exponentially as $q \to 0$. Then at small values of q, the pole in the complex plane v_x, $v_x = ip/q$, will be rather close to the real axis. We shall bypass the pole in integral (90.18) along the small semicircle [Fig. 111 (*b*)]. In the limit Re $p \to 0$ the integral along the straight segments will be real and approximately equal, as in the previous calculation, to $-4\pi ne^2/mp^2$. The integral along the semicircle C is equal to the product of πi by the residue of the integrand at the pole $v_x = ip/q$. Therefore, we have the equation

$$1 + \frac{4\pi ne^2}{mp^2} + \frac{i4\pi^2 e^2}{q^2 m} \frac{\partial f_0}{\partial v_x}\Big|_{ip/q} = 0. \qquad (90.22)$$

Let us put $p = i\omega - \gamma$ $(0 < \gamma \ll \omega)$ and calculate γ in the first not vanishing approximation. A simple calculation yields

$$\gamma = \sqrt{\pi}\, \frac{\omega_0^4}{q^3} \left(\frac{m}{2\pi}\right)^{3/2} e^{-m\omega_0^2/2Tq^2}. \qquad (90.23)$$

This expression can also be written in the form

$$\gamma = \sqrt{\frac{\pi}{8}}\, \omega_0 (qr_D)^{-3} \exp\left[-\frac{1}{2}(qr_D)^{-2}\right]. \qquad (90.24)$$

The decrement of damping turns out to be exponentially small at $qr_D \ll 1$, just as it was assumed in the calculation. At $qr_D \gtrsim 1$, γ proves to be comparable with ω_0 and, consequently, the longitudinal waves of a wavelength of the order of r_D and below are damped very rapidly and cannot practically propagate in plasma. The damping described by formulae (90.23) and (90.24) is called the *Landau damping*.

The physical origin of the Landau damping can be understood from the following reasoning (we follow here the treatment outlined in [43]). Let us consider in plasma the electrons for which the velocity projection on the direction of wave propagation is close to the wave phase velocity, $v_x \sim \omega_0/q$. "Colliding "with the wave hump, the electrons are reflected from it and change their energy. Upon such reflection the relative velocity of an electron and of the wave v_x

$-\omega/q$ changes the sign and becomes $\omega/q - v_x$, and the projection of the absolute velocity becomes equal to $2\omega/q - v_1$. For this reason the change in the electron energy due to "collision" with the hump of the wave is equal to

$$\Delta\varepsilon = \frac{m}{2}\left[\left(2\frac{\omega}{q} - v_x\right)^2 - v_x^2\right] = 2m\frac{\omega}{q}\left(\frac{\omega}{q} - v_x\right).$$

It is clear from this that at $v_x > \omega/q$ electron "overtakes" the wave and $\Delta\varepsilon < 0$—the electron loses a fraction of the energy, transferring it to the wave; at $v_x < \omega/q$ the wave "overtakes" the electron and $\Delta\varepsilon > 0$—in the case of such collisions the electrons acquire energy, taking it from the wave.

If electron velocity distribution follows the Maxwell velocity distribution, $n(v_x) \propto e^{-mv_x^2/2T}$, then in equal velocity ranges the number of slow electrons that take the energy from the wave is greater than the number of fast electrons that impart the energy to the wave. Consequently, processes in the course of which the wave losses energy prevail on the whole, and this explains qualitatively the Landau damping. It should be noted that if the velocity distribution of electrons differs from the Maxwell velocity distribution and there are sections on the curve representing the distribution function on which $dn/dv_x > 0$, processes of "build up" of oscillation prevail, in the course of which energy will be transferred from electrons to the wave.

We have limited ourselves so far to the consideration of single collisions between electrons and a wave. Actually, in a sine wave $\mathscr{E} = \mathscr{E}_0 \sin(qx - \omega t)$ electrons of a suitable velocity interval can oscillate between two humps of the wave, and if the shape of the wave does not change during one oscillation, there will be no damping, since the electrons will now transfer, now acquire energy, being reflected from two opposite humps. The frequency of electron's oscillations between two humps is $\Omega \sim \sqrt{\frac{e\mathscr{E}_0}{m\lambda}} \sim \sqrt{\frac{e\mathscr{E}_0}{m}q}$. The condition for the damping to exist consists in that the damping coefficient must exceed Ω, $\gamma > \sqrt{e\mathscr{E}_0 q/m}$. Since, according to formula (90.24), damping becomes material at $q \sim r_D^{-1} \sim \omega_0\sqrt{m/T}$ and at the same time $\gamma \sim \omega_0$, we obtain the inequality $T \gg e\mathscr{E}_0/q$, from which it follows that Landau's damping exists only in sufficiently weak fields; the energy gained by an electron along a distance of the order of the wavelength must be small compared with the mean thermal energy.

91. The Laws of Conservation and the Entropy Increase Law

In this and in the following sections we shall return to the analysis of the Boltzmann kinetic (transport) equation, which permits the derivation of a number of important corollaries concerning the change

in the mean values of physical quantities in space and in time. Let there exist some physical quantity ψ associated with a molecule, assumed by us to be a function of a point in the μ-space and time, $\psi = \psi(\mathbf{r}, \mathbf{v}, t)$. Let us find the value of ψ averaged over velocities. By definition,

$$\overline{\psi(\mathbf{r}, t)} = \frac{\int \psi(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}, t) d^3v}{\int f(\mathbf{r}, \mathbf{v}, t) d^3v},$$

or

$$n(\mathbf{r}, t) \overline{\psi(\mathbf{r}, t)} = \int \psi(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}, t) d^3v, \tag{91.1}$$

where $n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d^3v$ is the spatial particle density. Let us use the Boltzmann equation in the form

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} = \int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') (\tilde{f}\tilde{f}' - ff') d^3v' d^3\tilde{v} d^3\tilde{v}'.$$

We multiply both sides of this equation by $\psi(\mathbf{r}, \mathbf{v}, t)$ and integrate over $\mathbf{v}$, transforming the left-hand side of the equation obtained in the following manner:

$$\int \psi \left[\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} \right] d^3v$$
$$= \int \left\{ \frac{\partial}{\partial t}(f\psi) + v_k \frac{\partial}{\partial x_k}(f\psi) + w_k \frac{\partial}{\partial v_k}(f\psi) \right.$$
$$\left. - f \left[\frac{\partial \psi}{\partial t} + v_k \frac{\partial \psi}{\partial x_k} + w_k \frac{\partial \psi}{\partial v_k} \right] \right\} d^3v. \tag{91.2}$$

The third term on the right-hand side of expression (91.2) can be transformed by means of Gauss' theorem into a surface integral

$$\oint\!\!\!\oint f \psi w_k \, d\sigma_k$$

($d\sigma$ is an oriented surface element in the v-space), which vanishes when integrating over the entire velocity space, since $f(\mathbf{r}, \mathbf{v}, t) \cdot v^2 \to 0$ as $v \to \infty$.

In the first two terms the derivative symbols $\partial/\partial t$ and $\partial/\partial x_k$ can be taken out of the integral, and the entire left-hand side of Eq. (91.2) can be presented in the form

$$\frac{\partial}{\partial t}(n\overline{\psi}) + \frac{\partial}{\partial x_k}(n\overline{\psi v_k}) - \int f \left[\frac{\partial \psi}{\partial t} + v_k \frac{\partial \psi}{\partial x_k} + w_k \frac{\partial \psi}{\partial v_k} \right] d^3v. \tag{91.3}$$

Let us transform now the right-hand side, denoting by

$$I(\psi) = \int\int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') (\tilde{f}\tilde{f}' - ff') \psi(\mathbf{r}, \mathbf{v}, t) d^3v \, d^3v' \, d^3\tilde{v} \, d^3\tilde{v}'. \tag{91.4}$$

In formula (91.4) let us change the notation of integration variables by three methods:

$$\mathbf{v}\to\mathbf{v}', \quad \mathbf{v}'\to\mathbf{v}, \quad \tilde{\mathbf{v}}\to\tilde{\mathbf{v}}, \quad \tilde{\mathbf{v}}'\to\tilde{\mathbf{v}}'$$
$$\mathbf{v}\to\tilde{\mathbf{v}}, \quad \tilde{\mathbf{v}}\to\mathbf{v}, \quad \mathbf{v}'\to\tilde{\mathbf{v}}', \quad \tilde{\mathbf{v}}'\to\mathbf{v},$$
$$\mathbf{v}\to\tilde{\mathbf{v}}', \quad \tilde{\mathbf{v}}'\to\mathbf{v}, \quad \mathbf{v}'\to\tilde{\mathbf{v}}, \quad \tilde{\mathbf{v}}\to\mathbf{v}'.$$

Accounting for the symmetry properties of $P_1'(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')$, formulae (85.8) and (85.10), we obtain

$$I(\psi) = I(\psi') = -I(\tilde{\psi}) = -I(\tilde{\psi}') = \frac{1}{4}[I(\psi) + I(\psi') - I(\tilde{\psi}) - I(\tilde{\psi}')], \quad (91.5)$$

where

$$\psi = \psi(\mathbf{r}, \mathbf{v}, t), \quad \psi' = \psi(\mathbf{r}, \mathbf{v}', t),$$
$$\tilde{\psi} = \psi(\mathbf{r}, \tilde{\mathbf{v}}, t), \quad \tilde{\psi}' = \psi(\mathbf{r}, \tilde{\mathbf{v}}', t).$$

Finally, formulae (91.3) and (91.1) yield

$$\frac{\partial}{\partial t}(n\overline{\psi}) + \frac{\partial}{\partial x_k}(n\overline{\psi v_k}) - \int f\left[\frac{\partial\psi}{\partial t} + v_k\frac{\partial\psi}{\partial x_k} + w_k\frac{\partial\psi}{\partial v_k}\right]d^3v$$
$$= \frac{1}{4}\int\int\int\int P(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')(\tilde{f}\tilde{f}' - ff')$$
$$\times(\psi + \psi' - \tilde{\psi} - \tilde{\psi}')\, d^3v\, d^3v'\, d^3\tilde{v}\, d^3\tilde{v}'. \quad (91.6)$$

Equation (91.6), and also the equation with the non-symmetrized right-hand side

$$\frac{\partial}{\partial t}(n\overline{\psi}) + \frac{\partial}{\partial x_k}(n\overline{\psi v_k}) - \int f\left[\frac{\partial\psi}{\partial t} + v_k\frac{\partial\psi}{\partial x_k} + w_k\frac{\partial\psi}{\partial v_k}\right]d^3v$$
$$= \int\int\int\int P(\mathbf{v}, \mathbf{v}' \mid \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')(\tilde{f}\tilde{f}' - ff')\,\psi\, d^3v\, d^3v'\, d^3\tilde{v}\, d^3\tilde{v}' \quad (91.7)$$

is called the *Maxwell transport equation.*

Let us consider now particular cases: $\psi = m$, $\psi = mv_i$, $\psi = mv^2/2$. In all these cases the right-hand side of Eq. (91.6) vanishes during the impact by virtue of the laws of conservation of mass, momentum and energy. On the left-hand side of Eq. (91.6) we have:

for $\psi = m$,

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho\overline{v}_k) = 0; \quad (91.8)$$

for $\psi = mv_i$,

$$\frac{\partial}{\partial t}(\rho\overline{v}_i) + \frac{\partial}{\partial x_k}(\rho\overline{v_i v_k}) = F_i; \quad (91.9)$$

for $\psi = mv^2/2$,

$$\frac{\partial}{\partial t}\left(\frac{\rho\overline{v^2}}{2}\right) + \frac{\partial}{\partial x_k}\left(\frac{\rho\overline{v^2 v_k}}{2}\right) = \overline{v}_k F_k, \quad (91.10)$$

where ρ — mm — gas density;

F_i = force related to unit volume.

The physical meaning of the above relationships can readily be established. The quantities $\overline{\rho v_i}$, $\overline{\rho v_i v_k}$, $\overline{\rho v^2/2}$, $\overline{\rho v^2 v_k/2}$ are respectively the mean momentum, the mean projection of momentum flux, the mean kinetic energy, the mean projection of the flux of kinetic energy (all the quantities are related to unit volume). Equation (91.9) is the continuity equation for density and expresses the law of conservation of mass. Integrating Eq. (91.8) over some volume V and using the Gauss theorem, we find

$$\frac{d}{dt}\left(\int\int\int \rho\, d^3r\right) = -\oiint \rho v_k\, d\sigma_k, \qquad (91.11)$$

Equation (91.11) shows that the change in the quantity of substance in volume V per unit time is equa to the quantity of substance leaving or entering this volume per unit time.

Equation (91.9) is the momentum variation law. Integrating it over the volume V and using the Gauss theorem, we find the equation

$$\frac{d}{dt}\left(\int\int\int \overline{\rho v_i}\, d^3r\right) = -\oiint \overline{\rho v_i v_k}\, d\sigma_k + \int\int\int F_i\, d^3r, \qquad (91.12)$$

which shows that within the volume V momentum changes at the expense of momentum entering or leaving the volume V together with the gas flux, and also due to the action exerted on gas particles by an external force. Thus, Eq. (91.12) is the mathematical statement of Newton's second law of motion.

Finally, Eq. (91.10) represents the law of variation of the kinetic energy of a gas. Integrating this equation over the volume and using the Gauss theorem, we have

$$\frac{d}{dt}\left(\int\int\int \frac{\rho v^2}{2}\, d^3r\right) = -\oiint \frac{\overline{\rho v^2 v_k}}{2}\, d\sigma_k + \int\int\int F_k \overline{v_k}\, d^3r. \qquad (91.13)$$

Kinetic energy changes in volume V at the expense of its flowing into and out of the boundary of volume V (together with the gas flux) and at the expense of the work done by external forces.

Let us also derive the law of variation of the potential energy density $\rho\varphi(\mathbf{r})$, where $\varphi(\mathbf{r})$ is the potential energy per unit mass, assuming the forces acting on gas particles to be potential and conservative, so that $\rho F_k = -\partial\varphi/\partial x_k$ and $\partial\varphi/\partial t = 0$. Assuming in formula (91.6) $\psi = \varphi(\mathbf{r})$, we obtain

$$\frac{\partial}{\partial t}(\rho\varphi) + \frac{\partial}{\partial x_k}(\rho\varphi\overline{v_k}) = -F_k\overline{v_k}. \qquad (91.14)$$

The reader's attention should be drawn to the fact that the strength of the source of potential energy on the right-hand side of Eq. (91.14)

is equal and opposite in sign to strength of the source of kinetic energy in Eq. (91.10), which expresses the law of energy conservation: the total energy density $\rho\left(\frac{v^2}{2}+\varphi\right)$ has no sources.

Let us now use the kinetic equation to prove the theorem of increase in entropy upon the transition from a non-equilibrium state to an equilibrium one. This theorem, proved by L. Boltzmann, is called the *H-theorem*, since Boltzmann introduced instead of entropy the quantity H differing from entropy only in sign.

The proof of this theorem is also based on formula (91.6), but in this case the quantity $\psi(\mathbf{r}, \mathbf{v}, t)$ is chosen in a different way. For each gas particle the quantity $\psi(\mathbf{r}, \mathbf{v}, t)$ can be assumed to be one of its individual characteristics—mass m, momentum $m\mathbf{v}_i$ and kinetic energy $mv^2/2$ of the particle, independent of the state of other particles. When we pass to the description of the gas as a whole, these quantities are juxtaposed with macroscopic characteristics that change in time and from point to point, such as mass density $\rho(\mathbf{r}, t)$, momentum density $\rho\mathbf{v}$ and kinetic energy density $\rho v^2/2$.

It is, however, very important that for each particle the quantity $\psi(\mathbf{r}, \mathbf{v}, t)$ can be chosen to be a function depending not only on the velocity of this particle, but also on its position in space $\mathbf{r}$ and instant of time t. Moreover, the quantity $\psi(\mathbf{r}, \mathbf{v}, t)$ may contain information not only on the state of a given particle but, indirectly, also on the state of the gas as a whole, if it depends on coordinates, velocities and time through the distribution function $f(\mathbf{r}, \mathbf{v}, t)$, i.e. $\psi(\mathbf{r}, \mathbf{v}, t) = F[f(\mathbf{r}, \mathbf{v}, t)]$. As we have seen, in this more general case the variation of the function $\overline{\rho\psi(\mathbf{r}, \mathbf{v}, t)}$ and of its flux $\overline{\rho\mathbf{v}\psi(\mathbf{r}, \mathbf{v}, t)}$ in space and in time is also described by Eq. (91.6).

Let us now show that if each particle is juxtaposed with function $-\ln f(\mathbf{r}, \mathbf{v}, t)$ in the capacity of the quantity $\psi(\mathbf{r}, \mathbf{v}, t)$, then this function represents the "entropy" of the particle correct to a constant factor. This immediately follow from formula (63.12):

$$S = -\sum_{N, V, i} \frac{n}{L} \ln \frac{n}{L}.$$

Assuming in the above formula N and V to be fixed, replacing the probabilities n/L by the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ and passing from summation over i to integration over the μ-space, we obtain

$$S = -A \int f \ln f \, d^3v \, d^3r$$

where A is a constant.

From this it follows that for entropy density we have

$$\overline{ns(\mathbf{r}, t)} = -A \int f \ln f \, d^3v = -An\overline{\ln f}, \qquad (91.15)$$

and for the entropy flux density

$$\overline{nvs(\mathbf{r}, t)} = -A \int vf \ln f \, d^3v = -An\overline{v \ln f}. \tag{91.16}$$

Formulae (91.15) and (91.16) show that the expression $-A \ln f$ can be assumed to represent the entropy of a single particle.

Let us now return to Eq. (91.6) and assume $\psi = -\ln f(\mathbf{r}, \mathbf{v}, t)$. Then, the second term on the left-hand side of this equation vanishes. In fact, we have

$$\int f\left[\frac{\partial}{\partial t} + v_k \frac{\partial}{\partial x_k} + w_k \frac{\partial}{\partial v_k}\right] \ln f \, d^3v$$
$$= \int \left[\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k}\right] d^3v = \frac{\partial n}{\partial t} + \frac{\partial}{\partial x_k}(n\bar{v}_k) = 0$$

by virtue of continuity equation (91.8). Therefore, the above equation can be written in the form

$$\frac{\partial}{\partial t}(n\bar{s}) + \frac{\partial}{\partial x_k}(n\overline{sv_k})$$
$$= \frac{1}{4} \int\int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')(\tilde{f}\tilde{f}' - ff') \ln \frac{\tilde{f}\tilde{f}'}{ff'} d^3v \, d^3v' \, d^3\tilde{v} \, d^3\tilde{v}'. \tag{91.17}$$

Equation (91.17) has the form of the continuity equation for entropy density with sources on the right-hand side,

$$\frac{\partial}{\partial t}(n\bar{s}) + \frac{\partial}{\partial x_k}(n\overline{sv_k}) = Q, \tag{91.18}$$

in this case, by virtue of the evident inequality $(x - y) \ln (x/y) \geqslant 0$ the strength of the sources is non-negative, i.e. $Q \geqslant 0$. Integrating Eq. (91.18) over some fixed volume V and applying the Gauss theorem, we obtain

$$\frac{\partial}{\partial t}\left(\int\int\int n\bar{s} \, d^3r\right) = -\oint\oint n\overline{sv}_k \, d\sigma_k + \int\int\int Q \, d^3r. \tag{91.19}$$

According to Eq. (91.19), the entropy of a gas confined within volume V can change at the expense of entropy entering or leaving the considered volume with the gas molecules and increase at the expense of the entropy produced within the volume by entropy sources,

$$Q = \frac{1}{4} \int\int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}')(\tilde{f}\tilde{f}' - ff') \ln \frac{\tilde{f}\tilde{f}'}{ff'} d^3v \, d^3v' \, d^3\tilde{v} \, d^3\tilde{v}'. \tag{91.20}$$

In particular, for a closed system the entropy can only increase or remain constant, if the equality $\tilde{f}\tilde{f}' = ff'$ is satisfied.

Thus, we obtain the thermodynamic law of increase in entropy, with the kinetic derivation of this law giving us the expression for the sources of entropy, Eq. (91.20). For greater detail see Sec. 94.

92. Local Equilibrium

Let us find now the condition on which the entropy sources cease to produce entropy and equilibrium distribution sets in. It is clear from Eq. (91.20) that this condition is expressed by

$$\tilde{f}\tilde{f}' = ff'. \tag{92.1}$$

In this case, in Boltzmann's equation (see Sec. 85)

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} = \int\int\int P(\mathbf{v}, \mathbf{v}' | \tilde{\mathbf{v}}, \tilde{\mathbf{v}}') (\tilde{f}\tilde{f}' - ff') \, d^3v' \, d^3\tilde{v} \, d^3\tilde{v}'$$

the right-hand side vanishes and, consequently, the left-hand side vanishes too:

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + w_k \frac{\partial f}{\partial v_k} = 0. \tag{92.2}$$

Condition (92.1) can be written in the form

$$\ln \tilde{f} + \ln \tilde{f}' = \ln f + \ln f',$$

indicating that in respect to collisions the quantity $\ln f$ is an additive integral of motion. In the case of binary elastic collisions only five such integrals exist: three velocity components v_x, v_y, v_z, energy $\varepsilon = mv^2/2$ and the quantity independent of velocity. It can be shown (see, for instance, [1]) that no more additive integrals exist and that $\ln f$ can only be a linear combination of these quantities:

$$f = \exp[a + b_i v_i + cv_i^2]$$

(repeating indices imply summation). For our purpose it is convenient to write this expression in the following form:

$$f = \exp\left[a - \beta \frac{m}{2} (v_i - u_i)^2\right]. \tag{92.3}$$

In this form Eq. (92.3) can be interpreted as Maxwell's distribution with mean velocity components $\bar{v}_i = u_i$. The quantities a, β and u_i in Eq. (92.3) are generally functions of coordinates and time, since in the case of "instantaneous" collisions the coordinates undergo no discontinuity jumps, in distinction to velocity and energy. Therefore, at each point of space there exists a local mean velocity—the velocity of a gas flow, varying generally in time.

The function (92.3) will be denoted below by the symbol f_0 to emphasize that it characterizes a locally equilibrium state, and β will be shown to actually represent a distribution modulus connected with

temperature by the relation $\beta=1/T$, the quantities u_i have the meaning of components of local velocity of the gas flow. We shall also elucidate the meaning of the normalization factor e^{α}. It should be noted for this purpose that the function f_0 must satisfy the following three conditions:

$$\int d^3v\, f_0 = n, \qquad 1259$$

$$\int d^3v\, v_i f_0 = n\bar{v}_i,$$

$$\int d^3v\, \frac{m}{2}(v_i-\bar{v}_i)^2 f_0 = n\,\frac{\overline{m(v_i-\bar{v}_i)^2}}{2} = n\,\frac{3}{2}\,T. \tag{92.4}$$

Substituting (92.3) into these expressions and integrating, we obtain

$$e^{\alpha} = n\left(\frac{m\beta}{2\pi}\right)^{3/2}, \quad u_i=\bar{v}_i, \quad \beta=\frac{1}{T}. \tag{92.5}$$

Expression (70.3) for the function f_0 now acquires the form

$$f_0 = n\left(\frac{m}{2\pi T}\right)^{3/2}\exp\left[-\frac{m(v_i-u_i)^2}{2T}\right] \tag{92.6}$$

In addition, expression (92.3) must satisfy Eq. (92.2).

Substituting the expression for f_0 into Eq (92.2) and equating to zero in the obtained formula the coefficients at $v_k v_i^2$, $v_k v_i$, v_k and the terms not containing v_k, we obtain upon some transformations the following equations:

$$\frac{\partial\beta}{\partial x_k}=0, \tag{92.7}$$

$$\frac{\dot{\beta}}{\beta}\delta_{ik} = \frac{\partial u_i}{\partial x_i}+\frac{\partial u_k}{\partial x_i}. \tag{92.8}$$

$$F_k = m\left(\dot{u}_k+\frac{\dot{\beta}}{\beta}u_k\right)+\frac{1}{\beta}\frac{\partial}{\partial x_k}\left(a-\beta\,\frac{m}{2}u_i^2\right), \tag{92.9}$$

$$\frac{\partial}{\partial t}\left(a-\beta\,\frac{mu^2}{2}\right)+\beta u_k F_k = 0 \tag{92.10}$$

The first of these equations shows that in the expression for the Maxwell local distribution the quantity β, or temperature, is the same at all points of the space, but can change with time.

Equation (92.8) determines the local velocity field for a gas flow. Its general solution has the form

$$\mathbf{u} = \frac{\dot{\beta}}{2\beta}\mathbf{r}+[\boldsymbol{\omega}\mathbf{r}]+\mathbf{u}_{tr}(t), \tag{92.11}$$

where $\mathbf{u}_{tr}$ is the velocity of translatory motion. In fact, differentiating Eq. (92.8) with respect to x_l, we find

$$\frac{\partial^2 u_l}{\partial x_k \partial x_l} + \frac{\partial^2 u_k}{\partial x_l \partial x_l} = 0,$$

whence, upon a cyclic permutation of indices i, k, l, we obtain

$$\frac{\partial^2 u_r}{\partial x_k \partial x_l} = 0, \quad u_i + u_{tri} + \gamma_{ik} x_k.$$

Substituting this expression into Eq. (92.8), we have

$$\gamma_{ik} + \gamma_{ki} = \frac{\dot{\beta}\delta_{ik}}{\beta}, \quad \gamma_{ii} = \frac{\dot{\beta}}{2\beta}, \quad \gamma_{ik} = -\gamma_{ki} \quad \text{at} \quad i \neq k,$$

whence follows Eq. (92.11). Equation (92.11) satisfies Eq. (92.8) for ω, $\mathbf{u}_{tr}$ independent of coordinates, but arbitrarily depending on time. If the field in which the gas is placed is a potential one, i.e. $\mathbf{F} = -\nabla \mathcal{U}(\mathbf{r})$, then the angular velocity ω varies with time in proportion to temperature, $\omega(t)\,\beta(t) = \text{const}$. For a potential field Eq. (92.9) can be written in the form

$$\frac{\partial}{\partial t}(\beta \mathbf{u}) = -\frac{1}{m}\nabla\left[a - \beta\frac{mu^2}{2} + \beta\mathcal{U}(\mathbf{r})\right], \qquad (92.12)$$

whence

$$\operatorname{curl}\frac{\partial}{\partial t}(\beta \mathbf{u}) = \operatorname{curl}\left[\frac{\partial}{\partial t}(\beta[\boldsymbol{\omega}\mathbf{r}])\right] = 2\frac{\partial}{\partial t}(\beta\boldsymbol{\omega}) = 0,$$

so that $\beta\boldsymbol{\omega} = \text{const}$.

Thus, in the general case the macroscopic motion of a gas is the superposition of radial expansion (compression) with a velocity $\dot{\beta}\mathbf{r}/2\beta$, plane rotation with an angular velocity $\omega(t)$, which is the same at all points and varies in proportion to temperature, and translational motion with a velocity $\mathbf{u}_{tr}(t)$. However, all these three kinds of motion of a gas as a whole are impossible, if the gas is confined within a vessel. This is evident for radial expansion (compression) and translational motion, while "solid-state" rotation of the gas must damp due to the transfer of the torque to the walls of the vessel. In this case $\dot{\beta} = 0$, $\boldsymbol{\omega} = 0$ and $\mathbf{u}_{tr} = 0$, and, consequently, $\mathbf{u} = 0$. It follows then from Eqs. (92.9) and (92.10) that $\dot{a} = 0$ and $a = -\beta\mathcal{U}(\mathbf{r}) + \text{const}$ (if the external field is potential) and the distribution (92.3) degenerates into the ordinary Maxwell-Boltzmann distribution

$$f^{(0)} = \text{const}\exp\left[-\beta\left(\frac{mv^2}{2} + \mathcal{U}(\mathbf{r})\right)\right]. \qquad (92.13)$$

One can prove a more general statement: the local distribution degenerates into an equilibrium distribution, if the field is a potential one and the expansion of the potential in powers of x_i contains the terms

of the order of $x_i x_k x_l$ and higher, maybe along with the terms of lower powers (see the problem for this section). However, if the gas is not considered as a whole but only small volumes of it, then there can exist a state with a distribution function described by Eq. (92.6) with a density n depending on r and t and a flow velocity specified by formula (92.11); in this case β, $\mathbf{u}_{tr}$ and also ω can be slowly varying functions of coordinates. Although no rigorous proof of this statement has been found, it is usually assumed that in small volumes first a local Maxwell's distribution f_0 [(92.6)] sets in, then upon the elapse of a macroscopic relaxation time, the equilibrium Maxwell-Boltzmann distribution $f^{(0)}$ [(92.13)]. It should be emphasized that Boltzmann's kinetic equation does not describe this second stage of relaxation.

Let us now represent velocity v as the sum of two terms,

$$\mathbf{v}_i = \mathbf{u}_i + \mathbf{c}_i, \tag{92.14}$$

where, by definition,

$$\bar{\mathbf{v}}_i = \mathbf{u}_i, \quad \bar{\mathbf{c}}_i = 0. \tag{92.15}$$

From the point of view of mechanics, it is natural to interpret u as the velocity of the centre of inertia of a small volume of a gas, and c as the relative velocity of gas molecules. Statistical physics interprets u as the local velocity of macroscopic motion of a medium, and c as the velocity of random thermal motion of molecules. Then the equilibrium distribution becomes

$$f_0 = \exp\left[a - \frac{mc^2}{2T}\right]. \tag{92.16}$$

It should be noted that according to formula (92.16) the equilibrium (thermal) velocity distribution of molecules is always spherically symmetrical in the velocity space, since f_0 depends only on c^2.

Problem

Consider local equilibrium in a potential field

$$\mathcal{U}(r) = \mathcal{U}_0 + \alpha_i x_i + \alpha_{ik} x_i x_k + \alpha_{ikl} x_i x_k x_l$$

where if only some α_{ikl} differ from zero. Using Eqs. (92.9), (92.10) show that in such field $\dot{\beta} = 0$, $\omega = 0$, $u_{tr} = 0$, $u = 0$, $a = \text{const} - \beta\mathcal{U}(r)$ and that the local distribution (92.6) degenerates into the equilibrium Maxwell-Boltzmann distribution.

Hint. It is expedient to eliminate the expression $a - \beta\frac{mu^2}{2}$ from Eqs. (92.9), (92.10) and equate to zero the coefficients at the terms of the order of $x_i x_k$, x_i and x_i^2 in the resulting equation

93*. The Kinetic Equation for Plasma

In Sec. 90 we have considered the kinetic equation for plasma in a self-consistent field approximation with no account taken of particles' collisions. In this section we shall turn to examining the effects caused by collisions between particles and obtain the kinetic equation for plasma (Landay [44]) by transforming the collision integral in Boltzmann's equation.

Owing to the long-range nature of the Coulomb interaction, dominating in plasma are distant "collisions" with small scattering angles and transfer of momentum. This manifests itself, in particular, in the divergence of the total scattering cross section in a Coulomb field. Let us assume plasma to consist of m kinds of particles (electrons and different ions) and introduce partial distribution functions f_α ($\mathbf{r}_\alpha$, $\mathbf{p}_\alpha$, t) obeying the system of Boltzmann's equations. In this section the momentum $\mathbf{p}$ and not the velocity $\mathbf{v}_\alpha$ will be assumed to be the second argument of f_α:

$$\frac{\partial f_\alpha}{\partial t} + \mathbf{v}_\alpha \frac{\partial f_\alpha}{\partial \mathbf{r}_\alpha} + \mathbf{F}_\alpha \frac{\partial f_\alpha}{\partial \mathbf{p}_\alpha} = \sum_\beta J_{\alpha\beta}, \tag{93.1}$$

where the collision integrals $J_{\alpha\beta}$ are chosen according to formula (85.9) in the form

$$J_{\alpha\beta} = \int\int\int P(\mathbf{p}_\alpha, \mathbf{p}_\beta \mid \tilde{\mathbf{p}}_\alpha, \tilde{\mathbf{p}}_\beta)(\tilde{f}_\alpha \tilde{f}_\beta - f_\alpha f_\beta)\, d^3p_\beta\, d^3\tilde{p}_\alpha\, d^3\tilde{p}_\beta. \tag{93.2}$$

Let us introduce the notations $\tilde{\mathbf{p}}_\alpha = \mathbf{p}_\alpha + \Delta_\alpha$, $\tilde{\mathbf{p}}_\beta = \mathbf{p}_\beta + \Delta_\beta$, with $\Delta_\beta = -\Delta_\alpha$ due to momentum conservation; we represent the function of four vector arguments $P(\mathbf{p}_\alpha, \mathbf{p}_\beta \mid \tilde{\mathbf{p}}_\alpha, \tilde{\mathbf{p}}_\beta)$ as the function of the half sum and difference of the initial and final momenta $P'\left(\mathbf{p}_\alpha + \frac{1}{2}\Delta_\alpha, \mathbf{p}_\beta + \frac{1}{2}\Delta_\beta, \Delta_\alpha, \Delta_\beta\right)$. Due to symmetry properties, the function P is an even function of the last two arguments.

Since the main contribution to the integral $J_{\alpha\beta}$ is made by collisions with small momentum transfer, let us expand the transformed integrand of (93.2) into a series in Δ_α and Δ_β. It is clear that in this case the function P' must be expanded only in $\Delta_\alpha/2$ and $\Delta_\beta/2$ present in the first two arguments.

The terms of zeroth order in Δ_α and Δ_β cancell out and the first-order term, equal to

$$\int\int\int P'\left(f_\alpha \frac{\partial f_\beta}{\partial \mathbf{p}_\beta}\Delta_\beta + f_\beta \frac{\partial f_\alpha}{\partial \mathbf{p}_\alpha}\Delta_\alpha\right) d^3p_\beta\, d^3\Delta_\alpha\, d^3\Delta_\beta,$$

vanishes due to the fact that the function P' is even with respect to the last two arguments. The terms of second order in Δ_α, Δ_β are

equal to

$$\int\int\int d^3p_\beta\, d^3\Delta_\alpha\, d^3\Delta_\beta \left\{\left[\frac{\Delta_{\alpha i}\Delta_{\alpha k}}{2} f_\beta(\mathbf{p}_\beta)\frac{\partial^2 f_\alpha}{\partial p_{\alpha i}\partial p_{\alpha k}} + \Delta_{\alpha i}\Delta_{\beta k}\frac{\partial f_\alpha}{\partial p_{\alpha i}}\frac{\partial f_\beta}{\partial p_{\beta k}} + \frac{\Delta_{\beta i}\Delta_{\beta k}}{2} f_\alpha(\mathbf{p}_\alpha)\frac{\partial^2 f_\beta}{\partial p_{\beta i}\partial p_{\beta k}}\right] P' + \frac{1}{2}\left(\Delta_{\alpha i}\frac{\partial P'}{\partial p_{\alpha i}} + \Delta_{\beta i}\frac{\partial P'}{\partial p_{\beta k}}\right)\left(\Delta_{\alpha k} f_\beta\frac{\partial f_\alpha}{\partial p_{\alpha k}} + \Delta_{\beta k} f_\alpha\frac{\partial f_\beta}{\partial p_{\beta k}}\right)\right\}. \quad (93.3)$$

Let us transform the terms containing $\partial P'/\partial p_{\beta k}$, integrating them by parts, and take into account the fact that the surface integrals vanish in the $\mathbf{p}_\beta$-space because the function $f_\beta(\mathbf{p}_\beta)$ vanishes on an infinitely distant surface. We obtain for the integral $J_{\alpha\beta}$ the expression

$$J_{\alpha\beta} = \int\int\int d^3p_\beta\, d^3\Delta_\alpha\, d^3\Delta_\beta \left\{P'\left[\frac{\Delta_{\alpha i}\Delta_{\alpha k}}{2} f_\beta\frac{\partial^2 f_\alpha}{\partial p_{\alpha i}\partial p_{\alpha k}} + \frac{\Delta_{\alpha i}\Delta_{\beta k}}{2}\frac{\partial f_\alpha}{\partial p_{\alpha i}}\frac{\partial f_\beta}{\partial p_{\beta k}}\right] + \frac{\partial P'}{\partial p_{\alpha i}}\left[\frac{\Delta_{\alpha i}\Delta_{\alpha k}}{2} f_\beta\frac{\partial f_\alpha}{\partial p_{\alpha k}} + \frac{\Delta_{\alpha i}\Delta_{\beta k}}{2} f_\alpha\frac{\partial f_\beta}{\partial p_{\beta k}}\right]\right\}. \quad (93.4)$$

From this it is clear that the right-hand side of (93.1) can be written in the form of the divergence in the momentum space, $\partial j_{\alpha i}/\partial p_{\alpha i}$, where the flow density $j_{\alpha i}$ is expressed by the formula

$$j_{\alpha i} = \sum_\beta \frac{1}{2}\int\int\int d^3p_\beta\, d^3\Delta_\alpha\, d^3\Delta_\beta \times\left[\Delta_{\alpha i}\Delta_{\alpha k} f_\beta\frac{\partial f_\alpha}{\partial p_{\alpha k}} + \Delta_{\alpha i}\Delta_{\beta k} f_\alpha\frac{\partial f_\beta}{\partial p_{\beta k}}\right] P'. \quad (93.5)$$

Let us now return to the previous notation $P' = P(\mathbf{p}_\alpha, \mathbf{p}_\beta \mid \tilde{\mathbf{p}}_\alpha, \tilde{\mathbf{p}}_\beta)$ and recall (see Sec. 85) that the function P contains four delta-functions, ensuring the fulfillment of the laws of conservation of energy and momentum. Carrying out, as in Sec. 85, four integrations, replacing Δ_β by $-\Delta_\alpha$ and expressing the function $\Pi(\mathbf{p}_\alpha, \mathbf{p}_\beta \mid \tilde{\mathbf{p}}_\alpha, \tilde{\mathbf{p}}_\beta)$ in terms of the effective scattering cross section $d\sigma_{\alpha\beta}(q_{\alpha\beta}, \theta)$ we obtain for $j_{\alpha i}$ the following expression:

$$j_{\alpha i} = \frac{1}{2}\sum_\beta \int d^3p_\beta \left(f_\alpha\frac{\partial f_\beta}{\partial p_{\beta k}} - f_\beta\frac{\partial f_\alpha}{\partial p_{\alpha k}}\right) q_{\alpha\beta}\int \Delta_{\alpha i}\Delta_{\alpha k}\, d\sigma_{\alpha\beta}, \quad (93.6)$$

where $\mathbf{q}_{\alpha\beta}$ is the relative velocity of particles α and β.

So far, no use was made of the fact that the interaction between particles α and β is of the Coulomb kind. Turning to the evaluation of the integral $\int \Delta_{\alpha i}\Delta_{\alpha k} d\sigma_{\alpha\beta}$, we recall some information concerning Coulomb's collisions.

Let $\mathbf{q}_{\alpha\beta}$ and $\tilde{\mathbf{q}}_{\alpha\beta}$ denote the relative velocities of particles α and β before and after interaction, $\mathbf{q}_{\alpha\beta} = \mathbf{v}_\alpha - \mathbf{v}_\beta$ and $\tilde{\mathbf{q}}_{\alpha\beta} = \tilde{\mathbf{v}}_\alpha - \tilde{\mathbf{v}}_\beta$. By the law of conservation of energy,

$$\mu_{\alpha\beta} q_{\alpha\beta}^2/2 = \mu_{\alpha\beta} \tilde{q}_{\alpha\beta}^2/2,$$

where

$$\mu_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$$

is the reduced mass, we have $\tilde{q}_{\alpha\beta} = q_{\alpha\beta}$. Let us introduce the unit vector $\mathbf{n}$, which divides in two the angle between the asymptotes of

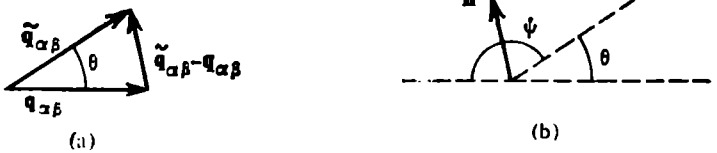


FIG. 112

the trajectory in the centre-of-mass system shown in Fig. 112. Then $\mathbf{q}_{\alpha\beta} - \tilde{\mathbf{q}}_{\alpha\beta} = 2\mathbf{n}(\mathbf{n}\mathbf{q}_{\alpha\beta})$, from which by the law of conservation of momentum we find

$$\Delta_\beta = -\Delta_\alpha = \mu_{\alpha\beta}(\mathbf{q}_{\alpha\beta} - \tilde{\mathbf{q}}_{\alpha\beta}) = 2\mu_{\alpha\beta} q_{\alpha\beta} \mathbf{n} \cos\psi. \qquad (93.7)$$

For Coulomb collisions we have, in addition, the ratio between the angle ψ and the impact parameter ρ [6]:

$$\rho = \frac{e_\alpha e_\beta}{\mu_{\alpha\beta} q_{\alpha\beta}^2} \tan\psi. \qquad (93.8)$$

Let us substitute expression (93.7) into the integral $\Lambda_{ik} = \int \Delta_{\alpha i} \Delta_{\alpha k} d\sigma_{\alpha\beta}$,

$$\Lambda_{ik} = 4\mu_{\alpha\beta}^2 q_{\alpha\beta}^2 \int n_i n_k \cos^2\psi \, d\sigma_{\alpha\beta}, \qquad (93.9)$$

and choose the polar axis along the vector $\mathbf{q}_{\alpha\beta}$; the angle φ will be measured from an arbitrary straight line perpendicular to $\mathbf{q}_{\alpha\beta}$. Then the projections of vector $\mathbf{n}$ on the direction of vector $\mathbf{q}_{\alpha\beta}$ and on two directions normal to it will be the quantities $\cos\psi$, $\sin\psi\cos\varphi$ and $\sin\psi\sin\varphi$. The differential cross section will be represented by $d\sigma_{\alpha\beta} = \rho \, d\rho \, d\varphi$. Then we obtain for Λ_{ik} the expression

$$\Lambda_{ik} = 4\mu_{\alpha\beta}^2 q_{\alpha\beta}^2 \int \cos^2\psi \rho \, d\rho \int_0^{2\pi} n_i n_k \, d\varphi.$$

Substituting the projections n_i, we can readily see that all non diagonal components of Λ_{ik} become zero and the two diagonal components, corresponding to the directions normal to $\mathbf{q}_{\alpha\beta}$, are the same

$$\int_0^{2\pi} \sin^2\varphi\, d\varphi = \int_0^{2\pi} \cos^2\varphi\, d\varphi = \pi,$$

and equal to ($i = 2, 3$)

$$\Lambda_{ii} = 4\pi\mu_{\alpha\beta}^2 q_{\alpha\beta}^2 \int \sin^2\psi \cos^2\psi \rho\, d\rho.$$

Expressing $\sin\psi$ and $\cos\psi$ in terms of ρ by formula (93.8), we find

$$\Lambda_{ii} = 4\pi \frac{\mu_{\alpha\beta}^4 q_{\alpha\beta}^6}{e_\alpha^2 e_\beta^2} \int \frac{\rho^3\, d\rho}{[1 + (\mu_{\alpha\beta}^2 q_{\alpha\beta}^4 / e_\alpha^2 e_\beta^2)\,\rho^2]^2}. \tag{93.10}$$

The integral in (93.10) diverges logarithmically at large ρ, which manifests the long-range nature of the Coulomb forces. It is, therefore, natural to truncate the integral at distances of the order of Debye's screening radius $r_D = [T/4\pi \sum_\alpha n_\alpha e_\alpha^2]^{1/2}$. Since the main contribution to this integral is made by large impact parameters, then correct to logarithmically large terms, we shall ignore unity in the integral denominator of (93.10) and introduce as the lower integration limit $\rho \sim |e_\alpha e_\beta|/\mu_{\alpha\beta} q_{\alpha\beta}^2 \sim |e_\alpha e_\beta|/T$ and as the upper integration limit $\rho \sim r_D$. Then we get for Λ_{ii} the expression

$$\Lambda_{ii} = 4\pi \frac{e_\alpha^2 e_\beta^2}{q_{\alpha\beta}^2} \ln \frac{r_D T}{|e_\alpha e_\beta|}. \tag{93.11}$$

The quantity $L = \ln r_D T/|e_\alpha e_\beta|$ is called the *Coulomb logarithm*. It has a low sensitivity to small changes in the lower and upper limits and has in typical cases rather large numerical values ($L \sim 10$ to 50). The diagonal component Λ_{11} is proportional to the integral converging in ρ:

$$\int \frac{\rho\, d\rho}{(1 + \mu_{\alpha\beta}^2 q_{\alpha\beta}^4 \rho^2 / e_\alpha^2 e_\beta^2)^2}.$$

and must be assumed equal to zero in our approximation. Thus, in the chosen system of coordinates Λ_{ik} is expressed by

$$\Lambda_{ik} = 4\pi e_\alpha^2 e_\beta^2 L \frac{q_{\alpha\beta}^2 \delta_{ik} - q_{\alpha\beta i} q_{\alpha\beta k}}{q_{\alpha\beta}^4}. \tag{93.12}$$

Indeed, expression (93.12) vanishes at $i \neq k$, since at least one projection $q_{\alpha\beta i}$ is equal to zero. It vanishes at $i = k = 1$, since $q_{\alpha\beta 1} = q_{\alpha\beta}$, and is equal to $4\pi e_\alpha^2 e_\beta^2/q_{\alpha\beta}^2$ at $i = k = 2$ or $i = k = 3$. By virtue of the tensor nature of Λ_{ik} expression (93.12) remains valid in any other system of coordinates.

Thus, we obtain for the current density in the momentum space the following expression:

$$j_{\alpha i} = \sum_{\beta} 2\pi e_\alpha^2 e_\beta^2 L \int d^3p_\beta \times \left(f_\alpha \frac{\partial f_\beta}{\partial p_{\beta k}} - f_\beta \frac{\partial f_\alpha}{\partial p_{\alpha k}} \right) \frac{q_{\alpha\beta}^2 \delta_{ik} - q_{\alpha\beta i} q_{\alpha\beta k}}{q_{\alpha\beta}^3}. \quad (93.13)$$

Application of Landau's equation will be illustrated by considering the problem of energy transfer from electrons to ions.

The index α will be used to denote quantities pertaining to electrons, and the index β, to ions. Let electrons and ions be described by Maxwell's equilibrium distribution functions with different temperatures T_α and T, assuming in this case that all kinds of ions are at the same temperature, since the ratio of energy transfer from one ion to another is much higher, due to the comparable magnitude of their masses, than the rate of energy transfer from electrons to ions:

$$f_\alpha = n_\alpha (2\pi m_\alpha T_\alpha)^{-3/2} \exp\left[-\frac{p_\alpha^2}{2m_\alpha T_\alpha} \right],$$
$$f_\beta = n_\beta (2\pi m_\beta T)^{-3/2} \exp\left[-\frac{p_\beta^2}{2m_\beta T} \right]. \quad (93\ 14)$$

In expression (93 13) for current density only the terms with $\beta \neq \alpha$ remain, since for identical particles the Maxwell distribution function turns the collision integral into zero.

Allowing for

$$\partial f_\alpha / \partial p_{\alpha i} = -p_{\alpha i} f_\alpha / m_\alpha T_\alpha, \quad \partial f_\beta / \partial p_{\beta k} = -p_{\beta k} f_\beta / m_\beta T,$$

we obtain for $j_{\alpha i}$ the expression

$$j_{\alpha i} = \sum_{\beta}{}' 2\pi e_\alpha^2 e_\beta^2 L \int d^3p_\beta f_\alpha f_\beta \left(\frac{v_{\alpha k}}{T_\alpha} - \frac{v_{\beta k}}{T} \right) \frac{q_{\alpha\beta}^2 \delta_{ik} - q_{\alpha\beta i} q_{\alpha\beta k}}{q_{\alpha\beta}^3} \quad (93.15)$$

(the prime at the summation sign denotes that there is no term with $\beta = \alpha$).

Transforming the term $v_{\beta k}/T = v_{\alpha k}/T - q_{\alpha\beta k}/T$ and allowing for $q_{\alpha\beta k}(q_{\alpha\beta}^2 \delta_{ik} - q_{\alpha\beta i} q_{\alpha\beta k}) = 0$, we can present Eq. (93.15) also in the form

$$j_{\alpha i} = \sum_{\beta}{}' 2\pi e_\alpha^2 e_\beta^2 L \int d^3p_\beta f_\alpha f_\beta \left(\frac{1}{T_\alpha} - \frac{1}{T} \right) v_{\alpha k} \frac{q_{\alpha\beta}^2 \delta_{ik} - q_{\alpha\beta i} q_{\alpha\beta k}}{q_{\alpha\beta}^3} \quad (93.16)$$

Let us assume electron velocities $v_{\alpha i}$ to be many times higher than the velocities of ions; due to the smallness of the mass ratio m_α/m_β,

this condition is usually well satisfied, even if the electron temperature T_α is one order higher than the ion temperature T. Then, in expression (93.16) $q_{\alpha\beta}$ can be replaced with a good accuracy by v

$$j_{\alpha i} = \sum_\beta{}' 2\pi e_\alpha^2 e_\beta^2 L \int d^3p_\beta f_\alpha f_\beta \left(\frac{1}{T_\alpha} - \frac{1}{T}\right) v_{\alpha k} \frac{v_\alpha^2 \delta_{ik} - v_{\alpha i} v_{\alpha k}}{v_\alpha^3}. \quad (93.17)$$

The change in the number of ions with momenta $p_{\beta i}$ per unit time is $\partial j_{\beta i}/\partial p_{\beta i}$, and the change in energy is equal to

$$\int \frac{p_\beta^2}{2m_\beta} \frac{\partial j_{\beta i}}{\partial p_{\beta i}} d^3p_\beta = -\int v_{\beta i} j_{\beta i} d^3p_\beta.$$

In consequence, the change in the kinetic energy of electrons is described by the equation

$$\frac{d}{dt}\left(\frac{3}{2} n_\alpha T_\alpha\right) = \sum_\beta{}' 2\pi e_\alpha^2 e_\beta^2 L \int\int d^3p_\alpha\, d^3p_\beta f_\alpha f_\beta \left(\frac{1}{T_\alpha} - \frac{1}{T}\right) v_{\beta i} v_{\beta k} \frac{v_\alpha^2 \delta_{ik} - v_{\alpha i} v_{\alpha k}}{v_\alpha^3}. \quad (93.18)$$

Integrating in Eq. (93.18) over the angles, we find

$$\int \frac{v_\alpha^2 v_\beta^2 - (v_\alpha, v_\beta)^2}{v_\alpha^3} d\Omega_\alpha = 2\pi \frac{v_\beta^2}{v_\alpha} \int_{-1}^{1} (1-\zeta^2)\, d\zeta = \frac{8\pi}{3} \frac{v_\beta^2}{v_\alpha};$$

then, the integral over momenta on the right-hand side of Eq. (93.1) acquires the form

$$\frac{8\pi}{3} \int d^3p_\beta f_\beta \frac{p_\beta^2}{m_\beta^2} \int_0^\infty dp_\alpha \frac{f_\alpha m_\alpha}{p_\alpha}.$$

Evaluating the integrals in this expression, we finally obtain the equation

$$\frac{dT_\alpha}{dt} = -\nu (T_\alpha - T),$$

where

$$\nu = \frac{8\sqrt{2\pi}}{3} \frac{m_\alpha^{1/2} e_\alpha^2 L}{T_\alpha^{3/2}} \sum_\beta{}' \frac{n_\beta e_\beta^2}{m_\beta}.$$

Problem

Find the energy flux carried by ions in plasma placed in a strong magnetic field H in the direction of temperature gradient ∇T (r) Larmor's frequency $\Omega_\beta = e_\beta H/m_\beta c$ is large compared with the characteristic collision frequency; in addition, it is assumed that ∇T (r) $\perp$ H.

Answer. In the first approximation in H^{-1}, the energy flux is perpendicular to ∇T and equal to

$$S^{(1)} = \frac{5n_\beta T}{2m_\beta \Omega_\beta}\left[\frac{\mathbf{H}}{H}, \nabla T\right],$$

in the second approximation,

$$S^{(2)} = -\chi \mid \nabla T \mid,$$

where $\chi = 8\sqrt{\pi}c^2 L n_\beta^2 e_\beta^2 m_\beta^{1/2}/T^{1/2}H^{-2}$; the heat capacity of plasma diminishes sharply in the direction perpendicular to the field intensity H.

94. Equations of Gas dynamics

Let us turn now to the consideration of the hydrodynamic stage in the evolution of a non-equilibrium system, assuming the state of the gas to be described with good accuracy by the first moments of a distribution function, and show how the Boltzmann kinetic equation permits derivation, in a rather general way, of the equations of classical gas dynamics. We shall proceed from the formulae derived in Sec. 91,

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho \bar{v}_k) = 0, \tag{94.1}$$

$$\frac{\partial}{\partial t}(\rho \bar{v}_i) + \frac{\partial}{\partial x_k}(\rho \overline{v_i v_k}) = \rho w_i = F_i, \tag{94.2}$$

$$\frac{\partial}{\partial t}\left(\frac{\rho \overline{v^2}}{2}\right) + \frac{\partial}{\partial x_k}\left(\frac{\rho \overline{v^2 v_k}}{2}\right) = \rho \bar{v}_k w_k = \bar{v}_k F_k, \tag{94.3}$$

describing the change in the gas density, momentum density and energy density. Let us make use of the decomposition of molecular velocity into the local velocity of the flow u_i and the random thermal velocity c_i, introduced in Sec. 92, and calculate the densities of the mass-, momentum-, and energy fluxes pertinent in these equations. We have

$$\rho \bar{v}_i = \rho u_i, \tag{94.4}$$

$$\rho \overline{v_i v_k} = \rho u_i u_k + \rho \overline{c_i c_k}, \tag{94.5}$$

$$\frac{\rho \overline{v^2 v_i}}{2} = \frac{\rho}{2}\overline{(u^2 + c^2 + 2u_k c_k)(u_i + c_i)}$$

$$= \frac{\rho}{2}(u^2 + \overline{c^2})u_i + \frac{\rho}{2}(\overline{c^2 c_i} + 2u_k \overline{c_i c_k}). \tag{94.6}$$

We introduce the notations

$$\rho \overline{c_i c_k} = P\delta_{ik} - \Pi_{ik}, \tag{94.7}$$

$$\frac{1}{2}\rho \overline{c^2 c_i} = L_i, \tag{94.8}$$

where P is pressure, and the meaning of the quantities Π_{ik}, L_i will be elucidated below. Since in an equilibrium state the distribution function f_0 depends only on c^2, by virtue of the fact that the integrand is odd, we find

$$\overline{\rho c^2 c_i} = \int f_0(c^2)\, c^2 c_i d^3c = 0$$

and, according to the known formula from the elementary kinetic theory of gases, $P = \rho\overline{c^2}/3$, we have

$$\overline{\rho c_i c_k} = \frac{1}{3}\rho\overline{c^2}\delta_{ik} = P\delta_{ik}.$$

In consequence, the tensor Π_{ik} and vector L_i vanish in the equilibrium state. If should be noted that the tensor Π_{ik} is symmetrical by definition, $\Pi_{ki} = \Pi_{ik}$; then, from Eq. (94.7) we get

$$\rho\tilde{U} = \frac{\rho\overline{c^2}}{2} = \frac{3}{2}P - \frac{1}{2}\Pi, \tag{94.9}$$

$$\Pi = \operatorname{Tr}\Pi_{ik} = \Pi_{ii}, \tag{94.10}$$

where $\rho\tilde{U}$ is the internal energy of unit volume. Allowing for the notations in formulae (94.7), (94.8), formulae (94.5) and (94.6) yield

$$\overline{\rho v_i v_k} = \rho u_i u_k + P\delta_{ik} - \Pi_{ik}, \tag{94.11}$$

$$\frac{\overline{\rho v^2}}{2} = \frac{\rho u^2}{2} + \rho\tilde{U}, \tag{94.12}$$

$$\frac{\overline{\rho v^2 v_i}}{2} = \frac{\rho u^2 u_i}{2} + Pu_i + \rho\tilde{U}u_i + L_i - \Pi_{ik}u_k. \tag{94.13}$$

Equations (94.1) through (94.3) now acquire the form

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho u_k) = 0, \tag{94.14}$$

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial}{\partial x_k}(\rho u_i u_k) = F_i - \frac{\partial P}{\partial x_i} + \frac{\partial\Pi_{ik}}{\partial x_k}, \tag{94.15}$$

$$\left\{\frac{\partial}{\partial t}\left(\frac{\rho u^2}{2}\right) + \frac{\partial}{\partial x_k}\left(\rho\frac{u^2 u_i}{2}\right)\right\} + \left\{\frac{\partial}{\partial t}(\rho\tilde{U}) + \frac{\partial}{\partial x_k}(\rho\tilde{U}u_k)\right\}$$
$$= F_k u_k - \frac{\partial}{\partial x_i}(L_i - \Pi_{ik}u_k) - \frac{\partial}{\partial x_i}(Pu_i). \tag{94.16}$$

Equation (94.14) represents the well-known continuity equation, expressing the law of conservation of mass.

The continuity equation permits an important transformation. Let there exist some quantity A depending on coordinates and time. We calculate its total derivative with respect to time, representing the complete change in the quantity A with time, result-

both from the change in A at the given point of space, $\partial A/\partial t$, and due to the change in coordinates with time:

$$\frac{\partial A}{\partial t}+\frac{\partial A}{\partial x_i}\frac{dx_i}{dt}=\frac{\partial A}{\partial t}+\frac{\partial A}{\partial x_i}u_i.$$

We transform this relationship, multiplying both sides by ρ, in the following manner:

$$\rho\left(\frac{\partial A}{\partial t}+\frac{\partial A}{\partial x_i}u_i\right)=\frac{\partial}{\partial t}(A\rho)+\frac{\partial}{\partial x_i}(A\rho u_i)-A\left(\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x_i}(\rho u_i)\right)$$

Since the last term on the right-hand side is identically equal to zero according to the continuity equation, we have

$$\rho\left(\frac{\partial A}{\partial t}+\frac{\partial A}{\partial x_i}u_i\right)=\frac{\partial}{\partial t}(A\rho)+\frac{\partial}{\partial x_i}(A\rho u_i). \qquad (94.17)$$

It should be noted that this technique, based on the law of conservation of mass, resembles the process of taking the mass out or introducing it into the time derivative, $m\frac{d\ldots}{dt}=\frac{d}{dt}(m\ldots)$ in Newton's equations, based on mass constancy. Using Eq.(94.17),Eq. (94.15) can be reduced to

$$\rho\frac{\partial u_l}{\partial t}+\rho u_k\frac{\partial u_l}{\partial x_k}=F_l-\frac{\partial P}{\partial x_l}+\frac{\partial \Pi_{lk}}{\partial x_k}. \qquad (94.18)$$

Equation (94.15) is the mathematical statement of Newton's second law for unit gas volume. Integrating both sides of this equation over some fixed volume V and making use of the Gauss theorem, we obtain

$$\frac{d}{dt}\left(\int\int\int \rho u_l d^3\rho\right)+\oiint \rho u_i u_k\, d\sigma$$

$$=\int\int\int \bar{F}_l d^3r+\oiint(\Pi_{lk}-P\delta_{lk})\,d\sigma_k. \qquad (94.19)$$

The left-hand side of Eq. (94.19) contains the change in momentum in volume V per unit time, resulting both from the change in momentum at a fixed point (the first term), and due to the motion of gas particles (the second term—momentum flux through the boundary of volume V).

The expression on the right-hand side of Eq. (94.19) represents the sum of the forces acting upon the volume under consideration. These forces include the external body force F_l (gravitational force, for instance) and the surface force $(\Pi_{ik}-P\delta_{ik})\,d\sigma_m$. In equilibrium $\Pi_{ik}=0$, and the surface force is perpendicular to the area $d\sigma$ and equal to $-Pd\sigma$.

In a non-equilibrium state the surface element $d\sigma$ is acted upon additionally by the force $dF_l=\Pi_{lk}d\sigma_k$, which has tangential com-

ponents (terms with $i \neq k$). These components represent, evidently, the viscous force. To single out these forces explicitly, it is convenient to represent the tensor Π_{ik} as the sum of two terms,

$$\Pi_{ik} = \Pi'_{ik} + \Pi''_{ik}, \tag{94.20}$$

where Π'_{ik} is the zero-trace of the viscosity tensor,

$$\Pi'_{ik} = M_{ik} - \frac{1}{3} M\delta_{ik}, \quad \operatorname{Tr} \Pi'_{ik} = \Pi'_{ii} = 0, \quad M = \operatorname{Tr} M_{ik} = M_{ii}, \tag{94.21}$$

and Π''_{ik} is its diagonal part,

$$\Pi''_{ik} = N\delta_{ik}. \tag{94.22}$$

The force due to the diagonal part Π''_{ik},

$$dF''_i = \Pi''_{ik}\, d\sigma_k = N\, d\sigma_i,$$

is orthogonal to the surface element $d\sigma$ and has no tangential components. The zero-trace Π'_{ik} causes both the appearance of an additional non-equilibrium pressure

$$dF'_i n_i = \Pi'_{ik} n_i\, d\sigma_k = \left(M_{ik} - \frac{1}{3} M\delta_{ik}\right) n_i\, d\sigma_k,$$

and the origination of forces tangential to the surface element viscous forces proper.

The reader's attention should be drawn now to the fundamental disadvantage of the system of macroscopic equations (94.14) through (94.16), consisting in that the system is open—there is less equations in the system than the number of unknown quantities. Indeed, the first equation of this system already contains four unknowns: density ρ and three velocity components u_i. The second vector equation (94.15) of the set only aggrevates the situation, since the number of equations rises to four, and six independent components of tensor Π_{ik} and the equilibrium pressure P are added to the number of unknown quantities. Thus we obtain four equations with eleven unknowns. It is clear that the addition of the scalar equation (94.16) to the system leads to similar results, since three projections of the heat conductivity vector L_i are added to the number of unknowns. We could compose equations of the (94.14) through (94.16) type even for higher velocity moments, choosing as the function ψ (r, v, t) in Eq. (94.6) or Eq. (94.20) the product of three, four, etc. velocity projections $v_i v_k v_l$, $v_i v_k v_l v_m$, etc. It is clear, however, that then new unknown tensors would appear on the right-hand side of corresponding equations with the number of components exceeding the number of new equations added.

One of the possible ways out consists in the use of intuitive phenomenological relationships connecting the fluxes of various physical quantities with the gradients of system's parameters. For in

stance, if for a gas not acted upon by external forces we introduce an assumption (confirmed experimentally) that macroscopic fluxes originate in the gas in the presence of a density gradient and that the flux velocity u_i is proportional to that gradient (*Fick's law*),

$$\rho u_k = -D \frac{\partial \rho}{\partial x_k}, \tag{94.23}$$

where D is the coefficient of diffusion, then Eq. (94.14) becomes

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x_k}\left(D \frac{\partial \rho}{\partial x_k}\right),$$

or, if D is assumed to be independent of coordinates,

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho. \tag{94.24}$$

Equation (94.24), referred to as the *diffusion equation*, contains only one unknown function $\rho(r, t)$. In this way, Eq. (94.14) can be made closed by postulating Fick's law and introducing the phenomenological coefficient of diffusion. It will be shown below that the system of equations (94.15) and (94.16) can be closed by postulating the phenomenological laws for viscosity and heat conductivity and introducing corresponding coefficients. It must be stressed, however, that such method of "closing" the system of macroscopic equations is only an apparent solution of the problem. In essence, using this method, we only take the difficulty to another place, since it becomes necessary to prove transport equations and find the transfer coefficients.

This can be accomplished by solving microscopic equations, for instance, the Boltzmann kinetic (transport) equation, which will be done in the next section. Here we limit ourselves to the elucidation of the following problem. It would appear that if Boltzmann's equation is solved and the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ is found, there is no need at all in the equations of gas dynamics, (94.14) through (94.16), since all moments of the distribution function ρ, ρu_i, $\rho u^2/2$, etc., can be calculated directly from their definitions.

Actually, however, the case is not as simple as it appears, since the approximate solutions of Boltzmann's equation can also depend on the gas dynamic variables such as ρ and u_i. For instance, if we are finding the distribution function in the vicinity of local equilibrium (usually, this is the case, as it will be shown in the next section), then, in the zeroth-order approximation the distribution function has the form

$$f_0 = n\left(\frac{m}{2\pi T}\right)^{3/2} e^{-m(v_i - u_i)^2/2T} \tag{94.25}$$

(see Sec. 92) and it depends on density n, flow velocity u and temperature T.

Let us return to the problem of "closing" Eqs. (94.15) and (94.16). In order to "close" these equations, the phenomenological expression for the tensor Π_{ik} must be postulated. In equilibrium Π_{ik} [illegible] and Eq. (94.15) represents the known *Euler's equation*

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_k}(\rho u_i u_k) + \frac{\partial P}{\partial x_i} = F_i \qquad (94.26)$$

for a compressible gas, if we add to it, as a second equation, the continuity equation in the general form, or for an incompressible fluid if we assume that $\rho = \text{const}$, $\partial u_i/\partial x_i = 0$ (condition for incompressibility). Below, for the sake of brevity, we shall always deal with a gas, although all the equations derived above describe in some approximation the flow of liquids.

In a non-equilibrium state account should be taken of the viscous friction forces. In the first approximation the components of tensor Π_{ik} must be proportional to the components of the gradient of velocity projections, since viscous friction originates between adjoining layers when the velocities of directional motion in these layers are different. Allowing for the symmetry conditions for the tensor Π_{ik} and dividing again the tensor into the zero-trace and diagonal parts we have

$$\Pi'_{ik} = \alpha\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \frac{2}{3}\frac{\partial u_l}{\partial x_l}\delta_{ik}\right), \qquad (94.27)$$

$$\Pi''_{ik} = \eta\frac{\partial u_l}{\partial x_l}\delta_{ik}, \qquad (94.28)$$

where the quantities α and η are referred to as the shear and bulk *viscosity coefficients* respectively, depending on the gas properties. In this approximation, for a viscous compressible gas Eq. (94.15) becomes

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial}{\partial x_k}(\rho u_i u_k) + \frac{\partial P}{\partial x_i} - \alpha\frac{\partial^2 u_i}{\partial x_k^2} - \left(\eta + \frac{1}{3}\alpha\right)\frac{\partial^2 u_k}{\partial x_i\, dx_k} = F_i, \qquad (94.29)$$

and for a viscous incompressible liquid the equation takes the form

$$\frac{\partial(\rho u_i)}{dt} + \frac{\partial(\rho u_i u_k)}{\partial x_k} + \frac{\partial P}{\partial x_i} - \alpha\frac{\partial^2 u_i}{\partial x_k^2} = F_i. \qquad (94.30)$$

Equations (94.29) and (94.30) are called the *Navier-Stokes equations*.

Thus, we arrived to a most important conclusion: in a thermodynamically equilibrium state all gases are inviscid. A gas can be considered to be compressible or incompressible depending on whether or not the quantity $\partial u_i/\partial x_i$ can be assumed to be equal to zero in a given problem. On the contrary, in a non-equilibrium state all gases are viscous, and the fact that tensor Π_{ik} differs from zero leads to two corollaries: the appearance of an additional non-equilibrium pressure and the origination of viscous friction forces specified by the zero-trace of tensor, Π'_{ik}.

Let us consider now Eq. (94.16). It is readily seen that it describes the variation of energy with time. Integrating both sides of this equation over some fixed volume and using the Gauss theorem, we obtain

$$\frac{d}{dt}\left(\int\int\int\left(\frac{\rho u^2}{2}+\rho\tilde{U}\right)d^3r\right)+\oiint\left(\frac{\rho u^2}{2}+\rho\tilde{U}\right)u_k\,d\sigma_k$$
$$=\int\int\int F_i u_i\,d^3r+\oiint(\Pi_{ik}-P\delta_{ik})\,u_k\,d\sigma_i-\oiint L_i\,d\sigma_i. \quad (94.31)$$

The left-hand side of Eq. (94.31) contains the total change in the energy confined within volume V per unit time. This energy consists of two parts: the kinetic energy $\rho u^2/2$ and the internal energy $\rho\tilde{U}$. The first term on the right-hand side represents the work done by the external body forces, and the second term, the work accomplished by surface forces, including the work of pressure forces (equilibrium pressure P and non-equilibrium viscosity tensor $\Pi = \mathrm{Tr}\,\Pi_{ik}$) and the work of viscous friction forces; by its mathematical structure the last term represents the flux of vector L_k through the boundary surface. It stipulates the change in energy in volume V even in the absence of external forces and viscous friction forces. Thus, this term can be interpreted as the flux of heat entering or leaving V per unit time due to heat conduction, and the vector L_k as the heat flux density vector.

To "close" Eq. (94.16), one must postulate the phenomenological expression for the vector L_k. Such a closing expression can be formulated on the basis of the following considerations.

Heat conduction is known to exist only in a non-equilibrium state, which agrees with empirical facts—heat transfer is impossible in the absence of a temperature gradient. In a first approximation the vector components must be proportional to the projections of the vector representing the temperature gradient

$$L_k=-\varkappa\frac{\partial T}{\partial x_k}, \quad (94.32)$$

where $\varkappa$ is the thermal conductivity, which depends on the properties of the fluid. Equation (94.32) is the formulation of *Fourier's law* of heat conduction.

Equation (94.31) can be presented in such a form that, in addition to the external forces, the left-hand side would contain only the quantities Π_{ik} and L_i that vanish in the equilibrium state. Taking the term $\oiint Pu_i\,d\sigma_i$ to the left-hand side, we obtain

$$\frac{d}{dt}\left[\int\int\int\left(\frac{\rho u^2}{2}+\rho\tilde{U}\right)d^3r+\oiint\left(\frac{\rho u^2}{2}+\rho\tilde{U}+P\right)u_i\,d\sigma_i\right]$$
$$=\int\int\int F_i u_i\,d^3r+\oiint\Pi_{ik}u_k\,d\sigma_i-\oiint L_i\,d\sigma_i. \quad (94.33)$$

Note that the second term on the left-hand side of Eq. (94.33) represents the enthalpy flux reduced to unit volume.

Equation (94.15) allows derivation of the law governing the variation of kinetic energy per unit volume of a fluid. We multiply both sides of this equation by u_i:

$$u_i\left[\frac{\partial(\rho u_i)}{\partial t}+\frac{\partial(\rho u_i u_k)}{\partial x_k}+\frac{\partial P}{\partial x_i}\right]=F_i u_i+\frac{\partial \Pi_{ik}}{\partial x_k}u_i. \quad (94.34)$$

Let us transform the first two terms on the left-hand side of Eq. (94.34) using (94.17)

$$u_i\left[\frac{\partial(\rho u_i)}{\partial t}+\frac{\partial(\rho u_i u_k)}{\partial x_k}\right]=\frac{\partial(\rho u^2)}{\partial t}+\frac{\partial(\rho u^2 u_i)}{\partial x_i}-\rho u_i\left(\frac{\partial u_i}{\partial t}+u_k\frac{\partial u_i}{\partial x_k}\right)$$
$$=\frac{\partial(\rho u^2)}{\partial t}+\frac{\partial(\rho u^2 u_i)}{\partial x_i}-u_i\left(\frac{\partial(\rho u_i)}{\partial t}+\frac{\partial(\rho u_i u_k)}{\partial x_k}\right).$$

This equation yields

$$u_i\left(\frac{\partial(\rho u_i)}{\partial t}+\frac{\partial(\rho u_i u_k)}{\partial x_k}\right)=\frac{\partial(\rho u^2/2)}{\partial t}+\frac{\partial(\rho u^2 u_i/2)}{\partial x_i}$$

and, upon substitution this into formula (94.34), we obtain the equation

$$\frac{\partial(\rho u^2/2)}{\partial t}+\frac{\partial(\rho u^2 u_i/2)}{\partial x_i}=F_i u_i+u_i\frac{\partial}{\partial x_k}(\Pi_{ik}-P\delta_{ik}). \quad (94.35)$$

It should be noted that according to Eq. (91.14) the term $-F_i u_i$ represents the density of the source of potential energy, and Eq. (94.35) can also be written in the form

$$\frac{\partial E}{\partial t}+\frac{\partial}{\partial x_i}(Eu_i)=u_i\frac{\partial}{\partial x_k}(\Pi_{ik}-P\delta_{ik}), \quad (94.36)$$

where E is the sum of the kinetic and potential energies per unit volume.

The right-hand side of Eq. (94.35), describing the variation of the kinetic energy density of a liquid, already contains only the work done by body and surface forces. Upon integration over the volume we find

$$\frac{d}{dt}\left(\int\int\int\frac{\rho u^2}{2}d^3r\right)+\oint\!\!\oint\frac{\rho u^2}{2}u_k\,d\sigma_k$$
$$=\int\int\int F_i u_i\,d^3r+\oint\!\!\oint(\Pi_{ik}-P\delta_{ik})\,u_i\,d\sigma_k. \quad (94.37)$$

Let us eliminate now from Eqs. (94.35) and (94.16) the terms containing the mechanical energy of fluid and derive the equation describing the variation of internal energy $\rho\tilde{U}$. Subtracting Eq. (94.35) from Eq. (94.16), we obtain

$$\frac{\partial(\rho\tilde{U})}{\partial t}+\frac{\partial(\rho\tilde{U}u_k)}{\partial x_k}=-\frac{\partial L_k}{\partial x_k}+(\Pi_{ik}-P\delta_{ik})\frac{\partial u_k}{\partial x_i}. \quad (94.38)$$

In the absence of fluxes ($u_l = 0$) Eq. (94.38) for an incompressible medium ($\rho = \text{const}$, $\tilde{U} = C_V T$) can be used to derive the heat-transfer equation

$$\rho C_V \frac{\partial T}{\partial t} = -\nabla L, \quad \frac{\partial T}{\partial t} = a^2 \nabla^2 T \left(a^2 = \frac{\varkappa}{\rho C_V} \right). \tag{94.39}$$

Integrating Eq. (94.38) over the volume, we have

$$\frac{d}{dt}\left(\int\int\int \rho \tilde{U}\, d^3r\right) + \oint\!\!\oint \rho \tilde{U} u_l\, d\sigma_l = -\int\int L_l\, d\sigma_l - \int\int\int P \frac{\partial u_l}{\partial x_l}\, d^3r + \int\int\int \Pi_{lk} \frac{\partial u_l}{\partial x_k}\, d^3r.$$

The above equation shows that, in addition to the convective energy flux through the boundary of the volume, represented by the second term on the left-hand side, the factors causing the change in the internal energy in volume V are the heat flux (the first term on the right-hand side), the work done by pressure forces (the second term on the right-hand side) and the work of viscous forces (the third term). Viscosity always causes a decrease in the mechanical and an increase in the internal energy, therefore the quantity $\Pi_{ik}(\partial u_l/\partial x_k)$ must be positive or equal to zero in the equilibrium state. Using formulae (94.27), (94.28), we find

$$\Pi_{ik} \frac{\partial u_i}{\partial x_k} = \alpha \left(\frac{\partial u_l}{\partial x_k} + \frac{\partial u_k}{\partial x_l} \right) \frac{\partial u_l}{\partial x_k} + \left(\eta - \frac{2}{3}\alpha \right) \frac{\partial u_l}{\partial x_l} \delta_{ik} \frac{\partial u_l}{\partial x_k} = \frac{1}{2}\alpha \left(\frac{\partial u_l}{\partial x_k} + \frac{\partial u_k}{\partial x_l} \right)^2 + \left(\eta - \frac{2}{3}\alpha \right) \left(\frac{\partial u_l}{\partial x_l} \right)^2.$$

In the above expression the first term is non-negative if $\alpha \geqslant 0$, and the second, when $\eta \geqslant 2/3\alpha$. Thus, the fact that the expression $\Pi_{ik}(\partial u_i/\partial x_k)$ is non-negative imposes certain restrictions on the quantities α and η.

Let us derive, finally, purely thermodynamically, the equation describing the variation of entropy, by introducing for this purpose the *hypothesis of local equilibrium*. Considering the state of the system to be non-equilibrium as a whole, we assume it possible to subdivide it into volumes so small (each of which, however, can be macroscopic) that each of these small volumes is in equilibrium and only the parameters describing the state (temperature, density, pressure, entropy, etc.) change slowly with time and from point to point.

This permits us to write the ordinary thermodynamic expression

$$d\tilde{S} = \frac{d\tilde{U}}{T} + \frac{P\, d\tilde{V}}{T} = \frac{d\tilde{U}}{T} - \frac{P}{T}\frac{d\rho}{\rho^2} \tag{94.40}$$

for the differential of local entropy of unit mass of a fluid. It is possible to use such a description due to the fact that, as will be

shown below [formula (94.43)] the capacity of entropy sources, violating the validity of relationship (94.40), is quadratic in gradients, resulting in that entropy generation can be ignored in the first approximation. Hence, we have

$$\frac{\partial \widetilde{S}}{\partial t} = \frac{1}{T}\frac{\partial \widetilde{U}}{\partial t} - \frac{P}{T\rho^2}\frac{\partial \rho}{\partial t},$$

$$u_k \frac{\partial \widetilde{S}}{\partial x_k} = \frac{u_k}{T}\frac{\partial \widetilde{U}}{\partial x_k} - \frac{P u_k}{T\rho^2}\frac{\partial \rho}{\partial x_k}.$$

Summing up these relationships, multiplying the equation obtained by ρ and using formula (94.17), we obtain

$$\frac{\partial(\rho\widetilde{S})}{\partial t} + \frac{\partial(\rho\widetilde{S}u_k)}{\partial x_k} = \frac{1}{T}\left[\frac{\partial(\rho\widetilde{U})}{\partial t} + \frac{\partial(\rho\widetilde{U}u_k)}{\partial x_k}\right] - \frac{P}{T\rho}\left(\frac{\partial \rho}{\partial t} + u_k\frac{\partial \rho}{\partial x_k}\right). \quad (94.41)$$

Let us transform the first term on the right-hand side of Eq. (94.41) with the aid of Eq. (94.38), and the second, with the aid of the continuity equation

$$\frac{\partial(\rho\widetilde{S})}{\partial t} + \frac{\partial(\rho\widetilde{S}u_k)}{\partial x_k} = \frac{1}{T}\left[-\frac{\partial L_k}{\partial x_k} + (\Pi_{ik} - P\delta_{ik})\frac{\partial u_k}{\partial x_i}\right] + \frac{P}{T}\frac{\partial u_k}{\partial x_k} = \frac{\Pi_{ik}(\partial u_k/\partial x_i) - \partial L_k/\partial x_k}{T} \quad (94.42)$$

The expression on the right-hand side of Eq. (94.42) is the density of entropy sources; it is seen to differ from zero only in the non equilibrium state, when heat conduction and viscosity exist. We integrate both sides of Eq. (94.42) over the volume:

$$\frac{d}{dt}\left(\int\int\int \rho\widetilde{S}\,d^3r\right) = -\oint\!\!\oint \rho\widetilde{S}u_k\,d\sigma_k - \oint\!\!\oint \frac{L_k\,d\sigma_k}{T} + \int\int\int \frac{\frac{\alpha}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right)^2 + \left(\eta - \frac{2}{3}\alpha\right)\left(\frac{\partial u_i}{\partial x_i}\right)^2}{T} d^3r. \quad (94.43)$$

The change in entropy in volume V of a fluid is seen to be the sum of three terms. The first term on the right-hand side of Eq. (94.43) represents the convective entropy flux, originating due to the entropy transport together with the mass of the fluid. The second term is due to heat conduction and represents the flux of entropy associated with the heat flux in accordance with the formula $d\widetilde{S} = \frac{\delta Q}{T}$. Depending on the direction of vector L_i, i.e. depending on the direction of the temperature gradient, this flux can be positive or negative just as the entropy flux due to convection. Finally, the third term

describes the origination of entropy due to viscous friction, and it is non-negative in accordance with the entropy increase law. We see this term to be proportional to the squares of velocity gradients, which justifies the assumption about the quasi-equilibrium nature of the process made in Eq. (94.40).

Thus, in a closed system, in which no convective entropy flux and heat flux exist (mass-impermeable and heat-insulated walls), entropy increases due to the irreversibility of the processes of viscous friction. If the system is in equilibrium, the second and third terms on the right-hand side of Eq. (94.43) are equal to zero, and entropy can only flow together with the fluid from point to point. In particular, in the case of impermeable walls the entropy in the volume V of a fluid remains constant.

The gasdynamic equations derived in this section contain maximum information on macroscopic motion of a gas that can be gained from Boltzmann's kinetic equation without solving it. In this case there appear in these equations three phenomenological coefficients of viscosity α and η and of thermal conductivity $\varkappa$, whose dependence on temperature and pressure remains unknown.

Assuming that the state of a moving gas deviates only slightly from equilibrium, we can find approximate solutions of Boltzmann's equation and substantiate the phenomenological transport equations (94.27), (94.28), (94.32), and also calculate the transfer coefficients.

95. Methods of Solution for Boltzmann's Equation

There exist several approximate methods of solution for Boltzmann's equation, all of them involving rather cumersome and long calculations that cannot be treated in detail in this book. A simplified version of one of these methods, namely, the *Enskog-Chapman method*, will be outlined below, as well as the essential reasonings followed in another solution method, referred to as the *Grad moment method*. A more detailed treatment of these calculations can be found in the special literature [40], [41], [45].

Let us consider a non-equilibrium state of a gas after the elapse of time large compared to the time of initial randomization, and assume that at each point of the vessel containing the gas a state sets in which is close to the local equilibrium state f_0 (Eq. (92.6)):

$$f_0 = n\left(\frac{m}{2\pi T}\right)^{3/2} \exp\left[-\frac{m(v_i - u_i)^2}{2T}\right]. \tag{95.1}$$

We shall assume, however, the time t to be small compared to the macroscopic relaxation time T^*, so that complete equilibrium, at which the Maxwell-Boltzmann distribution function becomes valid, has not set in. Let us look for a solution of Boltzmann's equation in

shown below [formula (94.43)] the capacity of entropy sources, violating the validity of relationship (94.40), is quadratic in gradients, resulting in that entropy generation can be ignored in the first approximation. Hence, we have

$$\frac{\partial \widetilde{S}}{\partial t} = \frac{1}{T}\frac{\partial \widetilde{U}}{\partial t} - \frac{P}{T\rho^2}\frac{\partial \rho}{\partial t},$$

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Summing up these relationships, multiplying the equation obtained by ρ and using formula (94.17), we obtain

$$\frac{\partial (\rho\widetilde{S})}{\partial t} + \frac{\partial (\rho\widetilde{S}u_k)}{\partial x_k} = \frac{1}{T}\left[\frac{\partial (\rho\widetilde{U})}{\partial t} + \frac{\partial (\rho\widetilde{U}u_k)}{\partial x_k}\right] - \frac{P}{T\rho}\left(\frac{\partial \rho}{\partial t} + u_k \frac{\partial \rho}{\partial x_k}\right). \quad (94.41)$$

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$$\frac{\partial (\rho\widetilde{S})}{\partial t} + \frac{\partial (\rho\widetilde{S}u_k)}{\partial x_k} = \frac{1}{T}\left[-\frac{\partial L_k}{\partial x_k} + (\Pi_{ik} - P\delta_{ik})\frac{\partial u_k}{\partial x_i}\right] + \frac{P}{T}\frac{\partial u_k}{\partial x_k} = \frac{\Pi_{ik}(\partial u_k/\partial x_i) - \partial L_k/\partial x_k}{T} \quad (94.42)$$

The expression on the right-hand side of Eq. (94.42) is the density of entropy sources; it is seen to differ from zero only in the non-equilibrium state, when heat conduction and viscosity exist. We integrate both sides of Eq. (94.42) over the volume:

$$\frac{d}{dt}\left(\int\int\int \rho\widetilde{S}\, d^3r\right) = -\oint\!\!\oint \rho\widetilde{S}u_k\, d\sigma_k - \oint\!\!\oint \frac{L_k\, d\sigma_k}{T} + \int\int\int \frac{\frac{\alpha}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right)^2 + \left(\eta - \frac{2}{3}\alpha\right)\left(\frac{\partial u_l}{\partial x_l}\right)^2}{T} d^3r. \quad (94.43)$$

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Let us consider a non-equilibrium state of a gas after the elapse of time large compared to the time of initial randomization, and assume that at each point of the vessel containing the gas a state sets in which is close to the local equilibrium state f_0 (Eq. (92.6)):

$$f_0 = n\left(\frac{m}{2\pi T}\right)^{3/2} \exp\left[-\frac{m(v_i - u_i)^2}{2T}\right]. \tag{95.1}$$

We shall assume, however, the time t to be small compared to the macroscopic relaxation time T^*, so that complete equilibrium, at which the Maxwell-Boltzmann distribution function becomes valid, has not set in. Let us look for a solution of Boltzmann's equation in

the form

$$f = f_0[1 + \varepsilon\varphi(\mathbf{r}, \mathbf{v}, t)], \tag{95.2}$$

assuming $\varepsilon \ll 1$, and present the Boltzmann equation as follows:

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + \frac{F_k}{m} \frac{\partial f}{\partial v_k} = \frac{1}{\varepsilon} J(f); \tag{95.3}$$

this is precisely the essence of the Enskog-Chapman approximation.

The introduction of the large dimensionless parameter ε^{-1} on the right-hand side of Eq. (95.3) implies that frequent collisions are assumed to be involved, by virtue of which the state of the gas is close to the local equilibrium. Substituting Eq. (95.2) into Eq. (95.3), we obtain in the zeroth order in ε the equation $J(f_0) = 0$, which is satisfied automatically (see Sec. 92), and in the first order in ε,

$$\frac{\partial f_0}{\partial t} + v_k \frac{\partial f_0}{\partial x_k} + \frac{F_k}{m} \frac{\partial f_0}{\partial v_k} = \int\int f_0 f_0' [\tilde{\varphi} + \tilde{\varphi}' - \varphi - \varphi'] q \, d\sigma \, d^3v'. \tag{95.4}$$

In order to avoid rather involved calculations and demonstrate the analysis only in principle, let us introduce a number of simplifying assumptions in solving Eq. (95.4). We shall assume that the gas is isothermal ($T = \text{const}$), incompressible ($\partial u_i/\partial x_i = 0$), external forces are absent ($F_i = 0$) and the pressure is constant ($\partial P/\partial x_i = 0$). With these assumptions we calculate the left-hand side of Eq. (95.4), using expression (95.1):

$$\frac{\partial f_0}{\partial t} + v_k \frac{\partial f_0}{\partial x_k} = \frac{m}{T}(v_k - u_k)\left[\frac{\partial u_k}{\partial t} + v_l \frac{\partial u_k}{\partial x_l}\right] f_0$$

$$= \frac{m}{T}(v_k - u_k)(v_l - u_l) \frac{\partial u_l}{\partial x_k} f_0. \tag{95.5}$$

Use was made of the fact that in the zeroth approximation in ε the Euler equation (94.26) is valid that at $F_i = 0$, $\rho = \text{const}$, $P = \text{const}$ and $\partial u_k/\partial x_k = 0$, has the form $\partial u_i/\partial t = -u_k \partial u_i/\partial x_k$. Symmetrizing Eq. (95.5), introducing relative velocities $c_i = v_i - u_i$ and making use of the incompressibility condition, let us write the right-hand side of Eq. (95.5) in the form*

$$f_0 \frac{m}{2T}\left(c_i c_k - \frac{1}{3} c^2 \delta_{ik}\right)\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right) = f_0 \frac{m\tilde{\Pi}_{ik}}{2T\alpha}\left(c_i c_k - \frac{c^2 \delta_{ik}}{3}\right).$$

* Attention of the reader should be drawn to the fact that no use is made of the phenomenological expression for the viscosity tensor (94.27), and only the notation $\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right) = \frac{\tilde{\Pi}_{ik}}{\alpha}$ is introduced. It will be shown below that $\tilde{\Pi}_{ik}$ is proportional to Π_{ik} and that the coefficient of viscosity is found.

Integral equation (95.4) reduces to

$$\frac{m}{2T}\left(c_i c_k - \frac{1}{3}c^2\delta_{ik}\right)\frac{\widetilde{\Pi}_{ik}}{\alpha} f_0 = \int\int f_0 f_0' (\varphi + \varphi' - \widetilde{\varphi} - \widetilde{\varphi}')\, q\, d\sigma\, d^3v'. \tag{95.6}$$

It is clear from the structure of Eq. (95.6) that the functions φ must be represented as the product of ψ_{ik} (v) and the velocity independent factor $\widetilde{\Pi}_{ik}/\alpha$:

$$\varphi(\mathbf{r},\ \mathbf{v},\ t) = \frac{\widetilde{\Pi}_{ik}}{\alpha}\psi_{ik}(\mathbf{v}). \tag{95.7}$$

Substituting Eq. (95.7) into Eq. (95.6), we find the equation for ψ_{ik} (v):

$$\frac{m}{2T}\left(c_i c_k - \frac{1}{3}c^2\delta_{ik}\right) f_0 = \int\int f_0 f_0' (\widetilde{\psi}_{ik} + \widetilde{\psi}_{ik}' - \psi_{ik} - \psi_{ik}')\, q\, d\sigma\, d^3v'.$$

Passing to integration over d^3c' on the right-hand side of this equation and assuming ψ, q and f_0 to be functions of c_i, we obtain

$$\frac{m}{2T}\left(c_i c_k - \frac{1}{3}c^2\delta_{ik}\right) f_0 = \int\int f_0 f_0' (\widetilde{\psi}_{ik} + \widetilde{\psi}_{ik}' - \psi_{ik} - \psi_{ik}')\, q\, d\sigma\, d^3c'. \tag{95.8}$$

The non-homogeneous integral equation (95.8) has solutions only when its left-hand side (non-homogeneity) is orthogonal to the solutions of the homogeneous equations. These solutions are represented by the additive integrals $\psi = 1$, $\psi = c_i$ and $\psi = c^2$ (see Sec. 91). The reader is advised to make sure (see problems to this section) that the left-hand side of Eq. (95.8) vanishes upon multiplication by 1, c_i, c^2 and integration over c_i.

The form of Eq. (95.8) suggests the necessity of looking for a solution in the form

$$\psi_{ik}(c) = D\left(c_i c_k - \frac{1}{3}c^2\delta_{ik}\right), \tag{95.9}$$

assuming D to be independent of c_i. To find this constant, we multiply both sides of Eq. (95.8) by $c_i c_k$ and integrate both sides over d^3c. A simple integration of the left-hand side yields

$$\frac{m}{2T}\int c_i c_k \left(c_i c_k - \frac{1}{3}c^2\delta_{ik}\right) f_0\, d^3c = \frac{m}{3T}\int c^4 f_0\, d^3c$$

$$= \frac{4\pi n}{3(2\pi)^{3/2}}\left(\frac{m}{T}\right)^{5/2}\int_0^\infty e^{-mc^2/2T} c^6\, dc = \frac{5nT}{m}. \tag{95.10}$$

Integration of the right-hand side is somewhat more involved. Substituting the values of f_0 and f_0' from Eq. (95.1) and of the function

ψ_{ik} from Eq. (95.9) and replacing $q = |\mathbf{c} - \mathbf{c}'|$ we obtain

$$n^2\left(\frac{m}{2\pi T}\right)^3 D \int\int\int \exp\left[-\frac{m(c+c'^2)}{2T}\right] c_i c_k \left[\tilde{c}_i \tilde{c}_k + \tilde{c}_i' \tilde{c}_k' - c_i c_k - c_i' c_k'\right| \times |\mathbf{c} - \mathbf{c}'| \, d\sigma \, d^3c \, d^3c' = n^2\left(\frac{m}{2\pi T}\right)^3 \int\int\int \exp\left[-\frac{m(c^2+c'^2)}{2T}\right] \times [(\mathbf{c}, \tilde{\mathbf{c}})^2 + (\mathbf{c}, \tilde{\mathbf{c}}')^2 - c^4 - (\mathbf{c}, \mathbf{c}')^2] \, |\mathbf{c} - \mathbf{c}'| \, d\sigma \, d^3c \, d^3c'. \quad (95.11)$$

The terms containing δ_{ik} cancell out since $c^2 + c'^2 = \tilde{c}^2 + \tilde{c}'^2$. Eliminating $\tilde{\mathbf{c}}'$ by the relationship $\tilde{\mathbf{c}}' = \mathbf{c} + \mathbf{c}' - \tilde{\mathbf{c}}$, we present the expression in the brackets in Eq. (95.11) in the form $2(\mathbf{c}, \tilde{\mathbf{c}} - \mathbf{c}') \times (\mathbf{c}, \tilde{\mathbf{c}} - \mathbf{c})$. The integral in Eq. (95.11) becomes equal to

$$2\int\int\int \exp\left[-\frac{m(c^2+c'^2)}{2T}\right] |\mathbf{c} - \mathbf{c}'| \, (\mathbf{c}, \tilde{\mathbf{c}} - \mathbf{c}') \, (\mathbf{c}, \tilde{\mathbf{c}} - \mathbf{c}) \, d\sigma \, d^3c \, d^3c' \quad (95.12)$$

and can be evaluated by passing to the centre-of-mass variables for molecules α and β according to the formulae

$$\mathbf{c} = \frac{\alpha+\beta}{2}, \quad \mathbf{c}' = \frac{\alpha-\beta}{2}, \quad \tilde{\mathbf{c}} = \frac{\alpha+\beta\nu}{2}, \quad \tilde{\mathbf{c}}' = \frac{\alpha-\beta\nu}{2}, \quad (95.13)$$

where ν is the unit vector $(\tilde{\mathbf{c}} - \tilde{\mathbf{c}}')/|\tilde{\mathbf{c}} - \tilde{\mathbf{c}}'|$. The transformation Jacobian (95.13) is equal to 1/8, and $d^3c \, d^3c' = 1/8 \, d^3\alpha \, d^3\beta$. The integral (95.12) takes the form

$$\frac{1}{64}\int\int\int \exp\left[-\frac{m(\alpha^2+\beta^2)}{4T}\right] \times \beta(\alpha+\beta, \beta\nu-\beta)(\alpha+\beta, \beta\nu+\beta) \, d\sigma \, d^3\alpha \, d^3\beta = \frac{1}{64}\int\int\int \exp\left[-\frac{m(\alpha^2+\beta^2)}{4T}\right] \times \beta[\beta^2(\alpha+\beta, \nu)^2 - (\alpha+\beta, \beta)^2] \, d\sigma \, d^3\alpha \, d^3\beta. \quad (95.14)$$

Let us introduce the spherical coordinates θ_α, φ_α, θ_β, φ_β of vectors α and β, choosing the direction of vector ν as the polar axis. The reader is to integrate by himself over θ_α, φ_α, θ_β, φ_β and show that expression (95.14) is equal to

$$-\frac{\pi}{12}\int_0^\infty e^{-m\alpha^2/4T}\alpha^2 \, d\alpha \int_0^\infty e^{-m\beta^2/4T}\beta^7 \, d\beta \int d\sigma. \quad (95.15)$$

For further transformation of expression (95.15) we must assume a definite value for $d\sigma$, depending on the law governing particles' interaction. We shall proceed from the model of hard spheres of radius a, not interacting at distances $r > a$. For this model $d\sigma = a^2 \sin\theta \, d\theta \, d\varphi$, where θ is the scattering angle. Integrating over θ, we obtain for Eq. (95.11) the value $-2^6\sqrt{\pi}a^2n^2(T/m)^{5/2}D$. Equating

it, according to Eq. (95.10), to the quantity $5Tn/m$, we get

$$D = -\frac{5}{2^5\sqrt{\pi}a^2n}\left(\frac{m}{T}\right)^{3/2}. \qquad (95.16)$$

Thus, in the first approximation the distribution function is equal to

$$f = f_0\left[1 - \frac{5}{2^5\sqrt{\pi}\,a^2n}\left(c_ic_k - \frac{1}{3}c^2\delta_{ik}\right)\frac{\widetilde{\Pi}_{ik}}{\alpha}\right]. \qquad (95.17)$$

According to definition (94.7), the components of tensor Π'_{ik} are expressed by

$$\Pi_{lm} = P\delta_{lm} - m\int c_lc_mf\,d^3c.$$

Here, account is taken of the fact that due to fluid incompressibility $\Pi'_{ik} = \Pi_{ik}$, $\Pi_{ll} = 0$. Substituting Eq. (95.17) and allowing for $\int c_lc_mf_0\,d^3c = P\delta_{lm}$, we find

$$\Pi_{lm} = \frac{5\left(\frac{m}{T}\right)^{3/2} m\widetilde{\Pi}_{ik}}{2^5\sqrt{\pi}\,a^2\alpha}\int c_lc_m\left(c_ic_k - \frac{1}{3}c^2\delta_{ik}\right)f_0\,d^3c \qquad (95.18)$$

(repeated indices imply summation). Let us integrate in Eq. (95.18) over the angles and take into account the readily proved relations

$$\int c_lc_m\,d\Omega = \frac{4\pi}{3}c^2\delta_{lm},$$

$$\int c_lc_mc_ic_k\,d\Omega = \frac{4\pi}{15}c^4[\delta_{lm}\delta_{ik} + \delta_{li}\delta_{km} + \delta_{lk}\delta_{im}].$$

Integrating in Eq. (95.18) now over c, we see that the quantities Π_{ik} and $\widetilde{\Pi}_{ik}$ are proportional to each other. In this way the empirical law of viscosity, expressed by Eq. (94.27), was derived from Boltzmann's equation and, equating Π_{ik} and $\widetilde{\Pi}_{ik}$, we obtain from Eq. (95.18) the expression for the coefficient of viscosity

$$\alpha = \frac{5}{2^5\sqrt{\pi}}\frac{(mT)^{1/2}}{a^2}. \qquad (95.19)$$

By analogy, it is possible to calculate the thermal conductivity coefficient for a gas with a temperature gradient, which for a hard-sphere gas is equal to

$$\varkappa = \frac{75}{2^7\sqrt{\pi}\,a^2}\left(\frac{T}{m}\right)^{1/2}. \qquad (95.20)$$

It should be noted that the ratio $\varkappa/\alpha$ turns out to be independent of temperature and equal to

$$\frac{\varkappa}{\alpha} = \frac{15}{4m} = \frac{5}{2}c_V, \qquad (95.21)$$

where $c_V = 3/2m$ is the specific heat of a monoatomic gas.

Formulae (95.19) through (95.21) agree with experiments only qualitatively, which is no wonder during to the large number of simplifications made in deriving them.

Another rather effective method of integrating Boltzmann's equation is the moment method (Grad's method). As has been already mentioned, by the moments of the distribution function are meant the integrals of the following form:

$$M^{(n)}_{i_1, i_2, \ldots, i_n} = \int f c_{i_1} c_{i_2} \ldots c_{i_n} d^3c.$$

The firsf moments are associated with the macroscopic characteristics of the gas, namely, Eqs. (94.7), (94.8) yield

$$M^{(0)} = \int f\, d^3c = n, \quad M^{(1)}_i = n\overline{c_i} = 0,$$
$$M^{(2)}_{ik} = n\overline{c_i c_k} = \frac{1}{m}(P\delta_{ik} - \Pi_{ik}), \quad M^{(3)}_{ikk} = n\overline{c_i c^2} = \frac{2}{m} L_i. \tag{95.22}$$

The main idea of the moment method consists in that the solution of Boltzmann's equation is found in the form of a series in the Hermite Chebyshev polynomials. It is convenient to write these polynomials in the form

$$H^{(n)}_{i_1, i_2, \ldots, i_n} = \frac{(-1)^n}{f_0} \frac{\partial^n f_0}{\partial c_{i_1} \partial c_{i_2} \ldots \partial c_{i_n}}, \tag{95.23}$$

where f_0 is the local Maxwell distribution (95.1). They satisfy the orthogonality conditions with weight f_0:

$$\int d^3c f_0 H^{(n)} H^{(m)} = 0 \quad (m \neq n). \tag{95.24}$$

Here are the values of several first Hermite polynomials

$$H^{(1)}_i = \left(\frac{m}{T}\right)^{1/2} c_i, \quad H^{(2)}_{ik} = \frac{m}{T} c_i c_k - \delta_{ik},$$
$$H^{(3)}_{ikl} = \left(\frac{m}{T}\right)^{3/2} c_i c_k c_l - \left(\frac{m}{T}\right)^{1/2} [c_i \delta_{kl} + c_k \delta_{il} + c_l \delta_{ik}]. \tag{95.25}$$

We are looking for a distribution function in the form

$$f = f_0 [1 + a_i H^{(1)}_i + a_{ik} H^{(2)}_{ik} + a_{ikl} H^{(3)}_{ikl} + \ldots]. \tag{95.26}$$

Using the orthogonality conditions (95.24), one can find the expansion coefficients of (95.26) and show that they are expressed in terms of moments $M^{(n)}$. So, for instance, for the first coefficients it is easy

to find the expressions

$$a_i = \int f_0 H_i^{(1)}\, d^3c = 0,$$

$$a_{ik} = \int f_0 H_{ik}^{(2)}\, d^3c = \int f_0 \left(\frac{m}{T} c_i c_k - \delta_{ik}\right) d^3c$$

$$= \frac{m}{T} M_{ik}^{(2)} = M^{(0)} \delta_{ik}. \qquad (95.27)$$

Substituting expansion (95.26) into Boltzmann's equation, multiplying both sides by Hermite polynomials $H^{(m)}$ and integrating over d^3c, we obtain a system of first-order differential equations, which is, generally speaking, infinite for the coefficients $a_{i_1, i_2, \ldots, i_n}$, and, consequently, for the moments $M_{i_1, i_2, \ldots, i_n}$. The exact solution of this system would be equivalent to the exact solution of the Boltzmann kinetic equation.

Since such an exact solution is impossible for real interaction models, expansion (95.26) is truncated to a finite number of terms, taking account in this expansion of only the moments having direct physical meaning. Such moments are $M^{(0)} = n$, $M_i^{(1)} = u_i$ (we have in mind $\int v_i f\, d^3\mathbf{v}$), $M_{ik}^{(2)}$ and $M_{ikk}^{(3)}$ related, according to formulae (95.22), to the tensor Π_{ik} and the heat flux vector L_i. The coefficients at higher-order moments are assumed to be equal to zero. Such approximation is referred to as the *thirteen-moment approximation* by the number of components $M^{(0)}$, $M_i^{(1)}$, $M_{ik}^{(2)}$ and $M_{ikk}^{(3)}$. In this approximation the system of differential equations for the moments becomes finite and can be solved with some degree of accuracy (see, for instance, [16], [41], [45]).

In many important practical problems, not requiring, however, a high accuracy, use is made of the so-called *relaxation-time approximation*. Let us consider first a spatially homogeneous gas in the absence of external forces. Then the kinetic equation takes the form

$$\frac{\partial f}{\partial t} = J(f) = \int\int (\tilde{f}\tilde{f}' - ff')\, q\, d\sigma\, d^3v'. \qquad (95.28)$$

Let us look for a solution close to the local equilibrium in the form

$$f = f_0 (1 + \varphi), \quad |\varphi| \ll 1. \qquad (95.29)$$

Ignoring second-order infinitesimals in φ, we obtain the equation

$$\frac{\partial \varphi}{\partial t} = \hat{R}\varphi = \int\int f_0' (\tilde{\varphi} + \tilde{\varphi}' - \varphi - \varphi')\, q\, d\sigma\, d^3v'. \qquad (95.30)$$

Let us establish some properties of the operator $\hat{R}$. Let the quantities $\lambda_i = -\tau_i^{-1}$ be the eigenvalues of this operator and $\psi_i(v)$ the eigenfunctions:

$$\hat{R}\psi_i(\mathbf{v}) = \lambda_i \psi_i(\mathbf{v}). \qquad (95.31)$$

The spectrum of eigenvalues contains the five-fold degenerate value $\lambda_0 = 0$ ($\tau_0 \to -\infty$), corresponding to five invariants of collisions $\psi_0^{(0)} = \text{const}$, $\psi_0^{(i)} = v_i$ ($i = 1, 2, 3$), $\psi_0^{(4)} = v^2$. The remaining eigenvalues λ_l will be shown to be negative ($\tau_l > 0$). Multiplying both sides of Eq (95.31) by $f_0\psi_l$ and integrating over v, we obtain

$$\lambda_l = \frac{\int f_0\psi_l \hat{R}\psi_l \, d^3v}{\int f_0\psi_l^2 \, d^3v} = \frac{\Lambda(\psi_l)}{\int f_0\psi_l^2 \, d^3v}.$$

Let us transform the numerator of the above expression, using the symmetry properties of the operator $\hat{R}$, following from definition (95.30). We have

$$\Lambda(\psi_l) = \Lambda(\psi_l') = -\Lambda(\tilde{\psi}_l) = -\Lambda(\tilde{\psi}_l')$$
$$= 1/4\,[\Lambda(\psi_l) + \Lambda(\psi_l') - \Lambda(\tilde{\psi}_l) - \Lambda(\tilde{\psi}_l')],$$

whence it follows that

$$\lambda_l = -\frac{\int\int\int f_0 f_0' (\psi_l + \psi_l' - \tilde{\psi}_l - \tilde{\psi}_l')^2 \, q \, d\sigma \, d^3v \, d^3v'}{\int f_0\psi_l^2 \, d^3v} \leqslant 0.$$

It can readily be verified that the functions ψ_l belonging to different eigenvalues, are orthogonal to each other with weight f_0.

Multiplying both sides of Eq. (95.31) by $f_0\psi_j$, integrating and changing the notation $i \rightleftarrows j$, we find

$$\int f_0\psi_j \hat{R}\psi_l \, d^3v = \lambda_l \int f_0\psi_j\psi_l \, d^3v,$$

$$\int f_0\psi_l \hat{R}\psi_j \, d^3v = \lambda_j \int f_0\psi_l\psi_j \, d^3v,$$

whence

$$(\lambda_l - \lambda_j) \int f_0\psi_l\psi_j \, d^3v = \int f_0 [\psi_j \hat{R}\psi_l - \psi_l \hat{R}\psi_j] \, d^3v = 0,$$

$$\int f_0\psi_l\psi_j \, d^3v = 0 \quad \text{at} \quad \lambda_l \neq \lambda_j.$$

Since the operator $\hat{R}$ is spherically symmetric in the velocity space its eigenfunctions have the form

$$\psi_{nlm}(v, \theta, \alpha) = R_{nl}(v) Y_{lm}(\theta, \alpha).$$

Here v, θ, α are spherical coordinates in the velocity space, $Y_{lm}(\theta, \alpha)$ are spherical functions, It follows from this that the eigenvalues λ_{nlm} are at least $(2l + 1)$-fold degenerate. Suppose that the operator $\hat{R}$ has only a discrete spectrum and functions ψ_l form a complete set Despite their high plausibility, these two statements have, evidently not been proved vigorously.

Let us look for a solution of Eq. (95.30) in the form of a series $\varphi = \sum_i c_i(t)\psi_i(v)$. Substituting into Eq. (95.30), multiplying by $\int_v \psi_j$ and integrating, we obtain, allowing for Eq. (95.31), $dc_j/dt = \lambda_j c_j = -c_j/\tau_j$, whence $c_j(t) = c_j^{(0)} e^{-t/\tau_j}$ and

$$\varphi = \sum_i c_i^{(0)} \psi_i(\mathbf{v})\, e^{-t/\tau_i}. \tag{95.32}$$

The quantities τ_i represent a set of relaxation time, and the coefficients $c_i^{(0)}$ are found from the initial conditions. At $c_i^{(0)} = \delta_{ik}$ we have $\varphi(t) = c_k^{(0)}\psi_k(v)\, e^{-t/\tau_k}$. If a maximum relaxation time τ exists and $\tau_i \ll t \leqslant \tau$, then

$$\varphi(t) \approx c_\tau \psi_\tau(v)\, e^{-t/\tau}.$$

In both cases only relaxation time is effective and the function $f(t)$ satisfies the equation

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau}. \tag{95.33}$$

Boltzmann's equation is, however, often used in this form without any rigorous substantiation even in the presence of inhomogeneity and external forces; then the equation is written in the form

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + \frac{F_k}{m}\frac{\partial f}{\partial v_k} = -\frac{f - f_0}{\tau}; \tag{95.34}$$

this is the essence of the τ-approximation, or the relaxation-time approximation.

This form of Boltzmann's equation can be substantiated more rigorously when the collisions between gas molecules can be ignored and the evolution of state is determined by collisions with particles of other kinds, considerably heavier than the gas molecules. Such particles can be molecules or atoms of impurities present in the gas, crystal lattice ions, if an electron gas in metal is involved, etc.

In this case the probability density of transition of a gas molecule from the state with velocity $\mathbf{v}$ to the state with velocity $\mathbf{v}'$ is equal to [see Eq. (68.52)]

$$\sigma(\mathbf{v}, \mathbf{v}')\, f(\mathbf{v})\, [1 \pm f(\mathbf{v}')] \tag{95.35}$$

where the upper sign pertains to a system of bosons and the lower, to a system of fermions. The dimension of the quantity $\sigma(\mathbf{v}, \mathbf{v}')$ is the reciprocal of time and depends on the mechanism of interaction between gas particles and heavy particles. The probability density of reverse transition has the form

$$\sigma(\mathbf{v}', \mathbf{v})\, f(\mathbf{v}')\, [1 \pm f(\mathbf{v})]. \tag{95.36}$$

Let us assume that due to the large mass of the heavy particles the collisions between them and gas particles are elastic, i.e. they take

place without energy transfer, so that $v' = v$. Then, by virtue of the principle of detailed balancing, $\sigma(\mathbf{v}, \mathbf{v}')$ is a symmetric function of its arguments. Indeed, in an equilibrium state, when $f(\mathbf{v}) = f_0(\mathbf{v})$, expressions (95.35), (95.36) must be equal to each other, whence it follows that

$$\sigma(\mathbf{v}', \mathbf{v}) = \sigma(\mathbf{v}, \mathbf{v}').$$

The collision integral can be obtained by subtracting Eq. (95.35) from Eq. (95.36) and integrating along all directions of $\mathbf{v}'$:

$$J = \int \sigma(\mathbf{v}, \mathbf{v}') [f(\mathbf{v}') - f(\mathbf{v})] \, d\Omega.$$

Then, the kinetic equation takes the form

$$\frac{\partial f}{\partial t} + v_k \frac{\partial f}{\partial x_k} + \frac{F_k}{m} \frac{\partial f}{\partial v_k} = J$$

and becomes linear.

Let the isotropy of the gas be disturbed by that an external field is directed along the z-axis or there exist the gradients of temperature, density and velocity of directional gas motion. In the state of equilibrium, the distribution function f_0 will then be a function of z and of absolute gas velocity v. The non-equilibrium distribution function remains a symmetric function of velocity projections ξ and η but can, evidently, depend on ζ. Thus, f will be a function of arguments z, v, ζ. For small deviations from equilibrium it is natural to look for f in the form

$$f = f_0 + \zeta f_1(z, v).$$

Substituting this expression into the collision integral, we obtain

$$J = f_1(z, v) \int \sigma(v, \theta) (\zeta' - \zeta) \, d\Omega,$$

where θ is the angle between the vectors $\mathbf{v}$ and $\mathbf{v}'$. It is clear that $\sigma(\mathbf{v}, \mathbf{v}')$ depends only on the modulus v and angle θ. We denote by α the angle between vector $\mathbf{v}$ and the z-axis and use φ to denote the angle between the planes (vOz) and (vOv'). Then, we have

$$\zeta = v \cos\alpha, \quad \zeta' = v(\cos\theta \cos\alpha + \sin\theta \sin\alpha \cos\varphi)$$

and, integrating over φ from 0 to 2π and over θ from 0 to π, we obtain

$$J = -\zeta f_1(z, v) \int_0^{\pi} \sigma(v, \theta) (1 - \cos\theta) \, 2\pi \sin\theta \, d\theta.$$

Denoting by τ^{-1} in the above expression the integral whose dimension is the reciprocal of time, we obtain the kinetic equation in the form (95.34).

Problems

1. Prove that the left-hand side of Eq. (95.8) vanishes upon multiplication by $\psi = 1$, c_i, c^2 and integration over d^3c.
2. Find the thermal conductivity and shear viscosity coefficients for the steady state of a Maxwell-Boltzmann gas in the τ-approximation, assuming temperature and velocity gradients to be independent of coordinates and the relaxation time to be constant.

Answer. $\varkappa = \frac{5nT\tau}{2m} = \frac{5P\tau}{2m}$, $\alpha = nT\tau = P\tau$.

3. Find in the τ-approximation the thermal conductivity and electric conductivity coefficients for an electron gas in a metal, assuming f_0 to be a Fermi quasi-equilibrium function, $f_0 = [e^{(\varepsilon-\mu)/T} + 1]^{-1}$, where $T = T(z)$ and $\mu = \mu[T(z)]$.

Hint. In problems 2 and 3, in the first approximation in $(f - f_0)/f_0$, f must be replaced by f_0 on the left-hand side of Boltzmann's equation, since the gradient $\partial f/\partial x_i$ and the forces F_i are assumed to be small for weak disturbances of equilibrium.

96. Irreversibility of Macroscopic Processes

We shall consider in this section the irreversible nature of the relaxation processes occurring in macroscopic systems. As has been already repeatedly noted (Sec. 82), the laws of both classical and quantum mechanics, governing the development of microprocesses in time, are invariant in respect to the change of the sign of time. This means that all microprocesses are reversible in principle, i.e. with an appropriate change of conditions (a change in the direction of initial velocities in classical mechanics) any microprocess can proceed in the forward and reverse directions, passing through the same intermediate states.

A question arises how can statistical physics, based on time-reversible laws of microprocesses, give the irreversible laws for macroscopic processes, in particular, the description of relaxation processes and the law of increase in entropy in closed systems. This question was raised directly in connection with the so-called *recurrence theorem* (Poincaré, Zermelo) according to which in a sufficiently long time the phase trajectory depicting the behaviour of a system in the Γ-space returns into the domain as close as desired to some initial point of this trajectory.

The proof of this theorem, based on the incompressibility property of the gas of representative points (Liouville's theorem) is almost evident. We shall consider macroscopic systems for which the constant-energy hypersurfaces in the Γ-space are closed and the

phase volume of states with an energy not exceeding E is finite and equal to $\Gamma(E)$. For real physical systems this condition is practically always satisfied. Let us consider inside $\Gamma(E)$ a small element of phase volume γ, $\gamma \ll \Gamma(E)$, and assume that representative points leave this volume per unit time, with some finite fraction of these points u_γ never returning into volume γ. In this case we immediately come to a contradiction, since in a sufficiently large time t the phase volume occupied by these points, $u_\gamma t$, would become larger than $\Gamma(E) - \gamma$, which is impossible due to the incompressibility property of the gas of representative points. Consequently, all the phase trajectories originating at the initial instant of time in volume γ (with the exception, perhaps, of a part of the trajectories whose initial points form a zero-dimensional set) must eventually return again and again into volume γ, and macroprocesses, just as microprocesses, should be strictly reversible.

Indeed, as has been already stated in Sec. 86, Liouville's equation, equivalent to equations of classical mechanics for systems of N material particles, is strictly reversible, i.e. if $F_N(\mathbf{r}, \mathbf{v}, t)$ is a solution of the tion

$$\frac{\partial F_N}{\partial t} + \hat{L}_N F_N = 0, \tag{96.1}$$

then $F_N(\mathbf{r}, \mathbf{v}, -t)$ is also a solution at approximately changed initial conditions, $F_N(\mathbf{r}, \mathbf{v}, 0) \to F_N(\mathbf{r}, -\mathbf{v}, 0)$. The chain of the Bogoliubov equations, strictly equivalent to Liouville's equation, also describes only reversible processes. Macroscopic processes become irreversible only at some later stages as a result of introduction of some (not arbitrary, as will be shown below) approximate methods of truncation for this chain of equations.

Thus, abstractly speaking, the evolution of the state of a macroscopic system is as reversible as microscopic processes. In particular, any non-equilibrium macroscopic state must recur sooner or later, no matter how great is the deviation from equilibrium. Let us consider two examples.

1. One half of a vessel, separated by a partition, is initially filled with gas. Then the partition is removed and we observe the expansion of the gas into a vacuum—the relaxation in the coordinate space.

2. A beam of "hot" molecules, having almost equal speeds $\mathbf{v}$, is introduced into a cold gas. Upon the elapse of some time the gas becomes "Maxwellian" due to molecular collisions and an equilibrium velocity distribution of molecules sets in. In accordance with the Poincare-Zermelo recurrence theorem, we can state that upon the elapse of some time the initial non-equilibrium state must recur with any desired accuracy, i.e. in the first example the gas must again be confined within one half of the vessel, and in the second example a beam of molecules with velocity $\mathbf{v}$ must form again.

However, such an abstract theoretical concept, associated with the recurrence theorem, in the case of large fluctuations, is only remotely related to reality, since for so large deviations from equilibrium as in the two examples considered above, the recurrence time is inconceivably large—many times greater not only than the age of the Earth, but also than the part of the Universe surrounding us.

The recurrence time can be roughly estimated in the following way. Let N molecules of a gas be confined within the volume V. By recurrence will be meant the repetition of the initial state of each molecule correct to Δv in velocity, Δx in coordinates. This accuracy corresponds to the volume $\Delta\Gamma$ of the phase space, $\Delta\Gamma = [\Delta v \Delta x]^{3N}$, while to the entire set of states of a gas with fixed energy

$$E = \frac{3}{2} NT = \sum_i \frac{mv_i^2}{2}$$

there corresponds a volume

$$\Gamma \approx C_{3N} \left(\sum_i v_i^2 \right)^{3N/2} V^N = C_{3N} \left(\frac{3NT}{m} \right)^{3N/2} V^N,$$

where $C_{3N} \approx (2\pi e/3N)^{3N/2}$ [see Mathematical Appendix, XIII, formula (XIII.10)]. Before returning to the initial position with the preset accuracy, a representative point must pass a number of states equal by the order of magnitude to $\Gamma/\Delta\Gamma$. Since the order of magnitude of the molecular mean free time $\tau \sim 1/d^2 n\bar{v} \sim V\overline{m/T}/d^2 n$ (d is the diameter of a molecule), we obtain the following estimate for the recurrence time τ_r:

$$\tau_r \sim \tau \frac{\Gamma}{\Delta\Gamma} \sim \left(\frac{V}{\Delta x^3} \right)^N \left(\frac{3\bar{N}T}{m\Delta v^2} \right)^{3N/2} \left(\frac{2\pi e}{3N} \right)^{3N/2} \tau$$

$$\sim \left(\frac{V}{\Delta x^3} \right)^N \left(\frac{T}{m\Delta v^2} \right)^{3N/2} \tau. \quad (96.2)$$

Let us determine now the recurrence to the initial state in an extremely "liberal" way, assuming Δx to be equal to 10% of interparticle distance, $\Delta x = 10^{-1} (V/N)^{1/3}$, and Δv equal to 10% of average velocity, $\Delta v = 10^{-1} (T/m)^{1/2}$. The situation would remain almost the same, if we replaced 10% by 50%, or even 90%. Then, formula (96.2) yields

$$\tau_r \sim \tau (10N)^N (10^2)^{3N/2} \sim \tau N^N.$$

For 1 cm^3 of a gas under standard conditions τ_r is so large that its ratio to the mean free time ($\tau \sim 10^{-6}$ s), to a second, to a year and to the lifetime of the surrounding us part of the Universe ($\sim 5 \times 10^9$ years) is almost the same (with logarithmic accuracy) and amounts to about $10^{2\times 10^{19}}$*.

* When faced with Zermelo's criticism of his concept of the irreversibility of macroprocesses, Boltzmann is reported to have laconically said: "Sie müssen zu lange warten" (You should wait too long).

Thus, the abstract theoretical reversibility is combined with the practical irreversibility of macroscopic processes when we speak of any considerable deviation from thermodynamic equilibrium. This practical irreversibility of macroscopic processes manifests itself in the absence of symmetry with respect to reflection in time (replacement of t by $-t$) of some kinetic equations, for instance, Boltzmann's equation. The indicated property stems from the fact that Boltzmann's equation describes the processes occurring only with an increase in entropy, but not with a decrease in it. Fokker-Planck's equation can be shown to possess the same property. This pertains the more so to equations of gas dynamics that are derived using phenomenological (irreversible) laws of diffusion, heat conduction and viscosity. Thus, for instance, it follows from the law of diffusion,

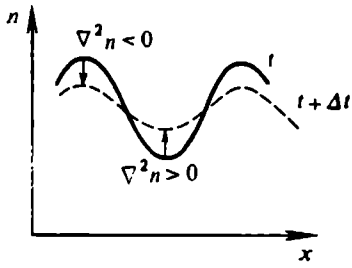

FIG. 113

$$\frac{\partial n}{\partial t} = D\nabla^2 n, \qquad (96.3)$$

that density n increases with time at points of the sgace where $\nabla^2 n > 0$, and decreases at the points where $\nabla^2 n < 0$. It is readily seen that this leads to equilibrium of gas density (Fig. 113). Reverse processes characterized by an increase in the density gradient and formation of "clots" and "rarefactions" in the gas are not described by Eq. (96.3).

A natural question arises: on what stage of transformation of the original reversible system of Bogoliubov's equations or equivalent to it Liouville's equation does the irreversibility appear of the equations?

The answer consists in the following: since the equations of mechanics are reversible, then irreversibility originates when we add to the equations of mechanics the probability hypotheses that are foreign to mechanics. In the case of Fokker-Planck's equation such hypothesis is the assumption about the Markovian nature of the process (Smoluchowski's equation). In deriving Boltzmann's equation from the chain of Bogoliubov's equations, the role of such a hypothesis is played by the condition of weakening of correlation (87.17), leading to the appearance of asymmetry in time reflection, etc. The introduction of such hypotheses is most closely associated with the role of particle interaction (in particular, with the role of collisions). It is the factor causing a directional evolution of a state which is described by a distribution function. It is, therefore, not by chance that irreversibility does not appear in kinetic equations in the derivation of which particle interaction, in particular, collisions, are ignored. Examples of such equations are the equation of a self-consistent

field (Sec. 89) and the equation of free-molecule flow (Sec. 88), the reversibility of which is readily observed.

The role of interaction between particles in the evolution of state can be revealed from a somewhat different angle. The most important characteristic of the equilibrium state of a closed system is the equal probability of equidimensional areas on the constant-energy hypersurface. It is exactly this property that guided us in the derivation of the Gibbs microscopic distribution in Sec. 61. For a system placed in a thermostat a similar statement consists in the equal probability of equal phase volumes confined within the thin energy layer, whose thickness is defined by energy fluctuation. The validity of all equilibrium distributions of statistical physics (canonical, grand canonical, etc), is based on this fundamental property. Meanwhile, no such equal probability of equal phase volumes exists in an arbitrary non-equilibrium state. For instance, in examples 1 and 2 considered above, the representative points occupy in the initial state only a part of the coordinate space (example 1) or of the momentum space (example 2).

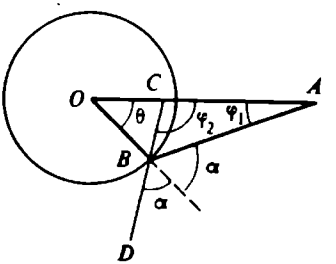

FIG. 114

It is clear that the interaction of particles with each other and with the thermostat must be such as to cause in the development of further evolution of state *mixing*, i.e. transition from the nonuniform distribution of representative points over the energy layer to a uniform distribution. The need for such mixing is already encountered in traditional problems in the theory of probability, for instance, for the equal probability of pulling any card from a pack of cards, the pack must be preliminary shuffled.

The need for mixing in problems in statistical physics was profoundly emphasized in the works of N. S. Krylov [46]. In this work, in particular, it was shown that in considering the process of "mixing" it becomes possible to introduce in a natural way and estimate the relaxation time as the time interval during which uniform spreading of the representative points over the constant-energy hypersurface or over the energy layer is attained. It is impossible to treat in some greater detail Krylov's work in this book and we shall limit ourselves, following [46], to an illustration of his ideas on the example of an ideal gas.

Let us assume molecules to be rigid spheres of radius r_0 and consider the collision of two molecules in the frame of reference in which the second molecule is fixed (Fig. 114).

In the figure, O is the centre of the fixed molecule, OB is its radius, A is the centre of the moving molecule, AB and BD preset the direction of motion of molecule A before and after collision (Fig. 114 is not drawn to scale, since $\lambda \gg r_0$). Let us find the relation between the angles φ_1 and φ_2 formed by the directions of molecular velocities before and after collision and the centre line of OA, assuming the distance AB traversed by molecule A before collision to be equal to the mean free path λ. According to the sine theorem, we find from triangle AOB

$$\frac{\sin \varphi_1}{r_0} = \frac{\sin \theta}{\lambda}. \tag{96.4}$$

Further, we have the equalities $2\alpha = \varphi_1 + \varphi_2$ and $\alpha = \theta + \varphi_1$ (2α and α are the exterior angles of triangles ACB and AOB respectively), whence we get $\theta = (\varphi_2 - \varphi_1)/2$. Substituting this into Eq. (96.4), we find

$$\varphi_2 = \varphi_1 + 2 \arcsin \left(\frac{\lambda}{r_0} \sin \varphi_1 \right), \tag{96.5}$$

whence

$$\frac{d\varphi_2}{d\varphi_1} = 1 + \frac{2 \dfrac{\lambda}{r_0} \cos \varphi_1}{\cos \left(\dfrac{\varphi_2 - \varphi_1}{2} \right)}. \tag{96.6}$$

Since for rarefied gases λ/r_0 is the large parameter and the averaged value of the factor $2 \cos \varphi_1/\cos [(\varphi_2 - \varphi_1)/2]$ is of the order of unity, this permits us to conclude that during the time of one collision the indeterminacy of the linear angle specifying the direction of molecular momentum increases in the order of magnitude λ/r_0 times. Since the momenta of two molecules change upon collision, the change in the solid angle, determining the direction of the vector of the $3N$-dimensional momentum, is proportional to $(\lambda/r_0)^2$. In time $\tau = \lambda/\overline{v}$ all N molecules of the gas undergo on the average one collision, and upon the elapse of time t, we obtain

$$\Delta\Omega_N = \Delta\Omega_N^{(0)} \left(\frac{\lambda}{r_0} \right)^{2Nt/\tau}. \tag{96.7}$$

Thus, the solid angle presetting the indeterminacy of the $3N$-dimensional momentum increases with time exponentially. The phase trajectories, initially originating from the small domain of the phase space or, more exactly, from the small area on the constant-energy hypersurface, move away from each other very rapidly and fill almost uniformly the entire hypersurface. According to Liouville's theorem, the original phase volume remains constant. In this case the constant-energy hypersurface will be, first roughly, then more and more finely, cut by the phase trajectories. In a certain time, characteristic of relaxation, rather small compared with Poincare's

recurrence time (see below), the probabilities of finding a representative point at similar sections of this hypersurface will become equal.

The momentum relaxation time or the time of "stirring" in the momentum space can be determined as the time it takes representative points to "spread" over the entire constant-energy sphere in momentum space, i.e. as the time in the course of which the solid angle $\Delta\Omega_N$ becomes equal in the order of magnitude to the total solid angle $\Omega_{3N} = (2\pi e/3N)^{3N/2}$ [see Mathematical Appendix, (XIII.13)].

We obtain for the relaxation time the expression

$$t_{\text{rel}} = \frac{\tau}{2N \ln(\lambda/r_0)} \ln \frac{\Omega_{3N}}{\Delta\Omega_N^{(0)}} \tag{96.8}$$

In order to estimate the quantity $\Delta\Omega_N^{(0)}$, let us consider a $3N$-dimensional sphere with radius P in the momentum space, where $P^2 = p_1^2 + p_2^2 + \ldots + p_N^2 \approx Np^2$ and p^2 is the mean square of the momentum of one particle.

The ratio $\Delta\Omega_N^{(0)}/\Omega_{3N}$ is equal to the ratio of the area of the domain of initial uncertainty in momentum $\Delta S_N^{(0)}$ to the total area of the $3N$-dimensional sphere S_{3N}. The quantity $\Delta S_N^{(0)}$, representing a $(3N-1)$-dimensional manifold with linear dimensions Δp, is expressed by $\Delta S_N^{(0)} \sim \Delta P^{3N-1}$, and $S_{3N} = (2\pi e/3N)^{3N/2} P^{3N-1}$ [see Mathematical Appendix; (XIII.12)]. Substituting these expressions into Eq. (96.8), we find correct to terms of the order of N^{-1}

$$t_{\text{rel}} = \frac{3\tau/2}{\ln(\lambda/r_0)} \ln \left[\frac{(2\pi e/3)^{1/2} p}{\Delta p} \right]. \tag{96.9}$$

The order of magnitude of the minimum value of Δp, admissible by the uncertainty relations, is $\hbar/L$, where L is the linear dimension of the vessel. Therefore for hydrogen at room temperature contained in a cube with an edge ~ 1 cm the argument of the logarithm in the numerator of Eq. (96.9) has the order of magnitude of 10^9. Under the same conditions, the order of magnitude of the logarithm argument in the denominator is $1/nr_0^3 \sim 10^3$, and we find the estimate for the momentum relaxation time to be $t_{\text{rel}} \sim (3 \text{ to } 5)\,\tau$. It should be noted that due to the logarithmic dependence on Δp, formula (96.9) has low sensitivity to the magnitude of the initial uncertainty in momentum, i.e. not only small but also large momentum fluctuations are "smoothed out" after a small number of collisions.

In a similar manner the concept of stirring also allows to estimate the relaxation time with respect to coordinates. It is clear that it must be defined as the time during which the order of magnitude of coordinate uncertainty becomes equal to the order of the size of the confining vessel (stirring in coordinate space)

$$\Delta x = \Delta x^{(0)} + \Delta v_{(x)}^{(0)} t = L. \tag{96.10}$$

Using the uncertainty relation $\Delta v_x^{(0)} \geqslant h/m\Delta x^{(0)}$, we obtain

$$\Delta x = \Delta x^{(0)} + \frac{ht}{m\Delta x^{(0)}} = L,$$

$$t = \frac{m\Delta x^{(0)}}{h}(L - \Delta x^{(0)}). \qquad (96.11)$$

Looking for the maximum of expression (96.11), we obtain $\Delta x_{max}^{(0)} = L/2$ and

$$t_{max} = mL^2/4h, \qquad (96.12)$$

which, in the conditions considered above, leads to the relaxation time of the order (10^2 to 10^3) s. It is clear that this calculation is associated with the estimate of the maximum relaxation time, compatible with the uncertainty relations, and the real relaxation time is many orders lower than the time specified by Eq. (96.12). For instance, when $\lambda > L$ and the velocities in the gas obey Maxwell's distribution, then $\Delta v^{(0)} \sim (T/m)^{1/2}$ and formula (96.10) yields the estimate

$$t \sim L\sqrt{\frac{m}{T}},$$

which in the same conditions leads us to the relaxation time of the order of 10^{-5} s. The "stirring" conditions were shown in [46] to hold for a wide class of macroscopic systems, embracing practically any physical systems encountered in statistical physics.

Thus, the evolution of an initially non-equilibrium state occurs in the following way. During relaxation time "stirring" of representative points in the energy layer of the Γ-space is accomplished and an "irreversible" process takes place with an increase in entropy. In the course of further evolution of the system, during time intervals exceeding many times the relaxation time, the system again returns to non-equilibrium states, in accordance with the recurrence theorem, and an observer will register the processes developing with a decrease in entropy. In the case of large fluctuations the recurrence time is large, exceeding by many orders the possible time of observation. System's evolution turns out to be practically irreversible in respect to such fluctuations. If we speak of small fluctuations, however, they can frequently repeat, and the more frequently, the smaller the scale of fluctuation. Then, during observation time, processes occurring with a decrease in entropy will be observed as often as process with an increase in entropy (Fig. 115), and the evolution becomes reversible. For a better understanding of the reasons for this dual nature of the system's evolution—irreversible in the case of small observation time and reversible at large—it is helpful to set forth another graphical interpretation.

In an energy layer E, $E + dE$ with a thickness of the order of energy fluctuation equilibrium (most probable) states occupy an almost the entire phase volume; in this case the greater the fluctuations that are assumed admissible in the equilibrium state, i.e. the rougher we specify the concept of equilibrium state, the greater the fraction of phase volume is occupied by the equilibrium macroscopic state (see problem 2 to this section).

Figure 116 shows a two-dimensional picture of a state of a system, on which non-equilibrium domains are represented by shaded areas and form only small "islands" in the entire volume $\Delta\Gamma(E)$. Micro-

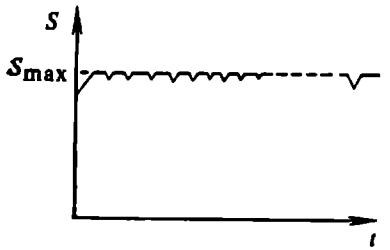

FIG. 115

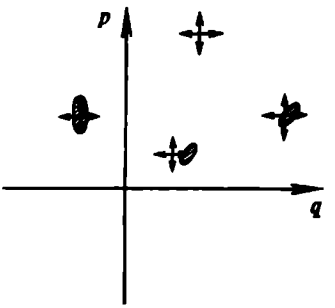

FIG. 116

processes in the system are reversible, i.e. forward and reverse displacements of a representative point are equally probable (Fig. 116). However, due to the fact that non-equilibrium states occupy in this figure only small "islands", a representative point positioned at the initial instant of time on one of these "islands" will leave it with a predominant probability and pass into the equilibrium domain. On the contrary, the point located at the instant of time $t = 0$ in the equilibrium domain will with a probability equal to unity, remain in this domain in the subsequent instants of time. This, naturally, is not in contradiction with the fact that the phase trajectory originating in any of the non-equilibrium islands, will again return into it upon the elapse of large time intervals, in accordance with the recurrence theorem. We arrive again at the conclusion that evolution is practically irreversible at small observation time, or when only large fluctuations are taken into account, and becomes reversible at large observation time or in respect to small fluctuations.

Let us consider, concluding this section, the concept known as the *thermal death of the Universe*. If the laws of statistical physics are assumed to be applicable not only to any finite system, but also to the entire Universe as a whole, then, in the time of its existence the Universe should have passed to a state of thermodynamic equilibrium

with uniform distribution of density, temperature and of the chemical composition, disturbed only by fluctuations. However, astronomical observations that embrace presently enormous regions of the Universe ($\sim 10^{10}$ light years, or 10^{23} km) indicate that no thermodynamic equilibrium exists in the region accessible to observation and that the state of the Universe is characterized by the presence of enormous gradients of density, temperature and chemical composition—stars and interstellar matter. Boltzmann put forward a hypothesis according to which this observable state of the Universe represents a giant fluctuation. This fluctuation hypothesis, however, meets the objection that the probability of such an enormous fluctuation is negligibly small and other fluctuations should have been observed with a much greater probability, for instance, one that would have ensured conditions in the solar system for the existence of observers of such fluctuations (intelligent life).

No answer has yet been given to the question raised before scientists about the absence of thermodynamic equilibrium in the observable part of the Universe, and we shall outline one of the attempts made to solve this problem.

The hypothesis explaining the reason for the lack of thermodynamic equilibrium has been approached in the Universe was put forward by I. P. Plotkin [47] and consists in the following. The microstates of the Universe and of any of its infinite parts form an infinite *countable* set, since each microstate can be assumed to be a cell in the μ-space and we can label all these cells in an arbitrary way. It will be shown below that the set of all microstates of a system, given by the occupation numbers N_1, N_2, . . . cells in the μ-space, is also infinite, but has the *power of a continuum*, i.e. it is equivalent to the continuous set of all real numbers of the arbitrary interval a, b. Due to the fact that of system's velocities are finite, the system remains in each microstate for a finite time. It follows from this that even during the infinite lifetime the Universe cannot pass through all conceivable states; moreover, the Universe can be merely in a negligible fraction of all possible states. From this it follows that one cannot speak of more or less probable states of the Universe, since these states do not recur and the concept of the thermodynamic state as the most probable state of the Universe is meaningless. The evolution of the Universe is not a directional, translational process, but represents rather a random change of states.

Let us prove now that the set of all microstates of infinite system has the power of a continuum. Let us consider the mappings of a natural number series on numbers 0 and 1, that contain an infinite set of zeros and unities. For instance,

$$\begin{array}{l} 1,\ 2,\ 3,\ 4,\ 5,\ 6,\ 7,\ 8,\ \ldots \\ 1,\ 0,\ 0,\ 1,\ 1,\ 0,\ 0,\ 0,\ \ldots \end{array} \qquad (96.13)$$

The set of all such mappings has the power of a continuum due to the fact that any decimal fraction from the interval 0, 1 can be written in the binary system [48]. Let us compare each element of this set or each mapping with the distribution of particles among states in accordance with the following law. In the first state there are the particles whose numbers are juxtaposed in the mapping (96.13) with the first N_1 zeros (for instance, if $N_1 = 4$, then these particles are labeled by 2, 3, 6, 7). In the second state there are the particles whose numbers are juxtaposed with the first N_2 unities (for instance, if $N_2 = 3$, then these particles are labeled by 1, 4, 5). In the third state there are the particles whose numbers are juxtaposed with the following N_3 zeros, etc. Let us set some definite sequence of numbers N_i. Then, for each mapping of the kind (96.13) there exists one and only one distribution of particles among states and, on the contrary, for each given particle distribution among states there corresponds one and only one mapping (96.13). Hence, there exists one-to-one correspondence between the two sets—the set of particle distributions among the states with preset N_i and the set of mappings of the kind (96.13), with the two sets having the power of a continuum.

Problems

1. Show with the aid of a one-dimensional Fokker-Planck's equation that the entropy of a closed system, specified by the formula $S = -\int f \ln f \, d^3v \, d^3r$, can only increase or remain constant.
2. The phase space of an ideal monoatomic gas is subdivided into cells with a phase volume γ_i ($i = 1, 2, \ldots, n$; $n \gg 1$). States with occupation numbers N_i have a phase volume $\Gamma(N_i) = N! \prod_{i=1}^{n} (\gamma_i^{N_i}/N_i!)$ (cf. Sec. 36); (a) for a fixed number of particles and energy ($\prod_i N_i = N$, $\sum_i N_i \varepsilon_i = U$), find the state with a maximum phase volume $\Gamma(N_i^{(m)}) = \max$; (b) show that the phase volume of states with occupation numbers differing from the most probable $N_i^{(m)}$ decreases following the Gauss exponential law, with increasing deviations.

Answer. (a) $N_i^{(m)} = \text{const}\, \gamma_i e^{-\beta\varepsilon_i}$ —Maxwell-Boltzmann's distribution; (b) $\dfrac{\Gamma(N_i^{(m)} + \Delta N_i)}{\Gamma(N_i^{(m)})} = \exp\left[-\dfrac{1}{2}\left(\dfrac{\Delta N_i}{N_i^{(m)}}\right)^2 N\right]$, for instance, for $\Delta N_i = 10^{-6} N_i^{(m)}$ and $N \approx 10^{19}$ we have for this relationship $e^{-1/2\times 10^7} \sim 10^{-3\times 10^6}$.

97*. Density Matrix and Its Variation with Time. The Kubo Method

In addition to solution methods for problems in kinetics considered in preceding sections, a rather fruitful quantum-mechanical method has been developed in the last few years, based on the use of the so-called *density matrix*.

Let us imagine a macroscopic subsystem which is a part of a total system (subsystem + surroundings). From the quantum-mechanical viewpoint it would be possible to describe the subsystem with the aid of the wave function depending on the coordinates of all system's particles, $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$, if an observer could measure the complete set of mechanical quantities describing the microstate of the subsystem. For macroscopic subsystems such measurement is practically impossible. Furthermore, if such a measurement were taken at the instant of time $t = 0$, the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, t = 0)$ could not be continued in time, for owing to the existence of interaction between subsystem's particles and surroundings only the wave function of the total system has a meaning.

In this connection the state of the macroscopic subsystem must be described not in terms of a wave function, but with the aid of another mathematical means, the density matrix. Let $\psi^{(i)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ represent a set of instantaneous "wave" functions of a subsystem in which the latter could be found, if there were no interaction between subsystem and the surroundings at the given instant of time. (The symbol (i) denotes here a set of quantum numbers determining the instantaneous state of the subsystem.) If no interaction took place later on as well, the subsystem would have a stationary wave function $\psi^{(i)}$. In this case the state is said to be pure. But in the real case of a subsystem interacting with the surroundings, we can only indicate for each of the pure states the statistical weights P_i with which they enter the true state of the subsystem, referred to as the mixed state in this case.

It should be stressed, however, that the coefficients P_i are then assigned not to the wave functions $\psi^{(i)}$, but to their bilinear combinations, since, due to the superposition principle, the combination $\sum_i P_i \psi^{(i)}$ would again represent a wave function and correspond to a pure state. For instance, the probability density for a definite system's configuration, which in a pure state is equal to $|\psi^{(i)}|^2$, in the mixed state is assumed to be equal to

$$\rho = \sum_i P_i |\psi^{(i)}|^2, \quad \sum_i P_i = 1, \tag{97.1}$$

and the mean value of the physical quantity L is equal to

$$\langle L \rangle = \sum_i P_i \bar{L}_i = \sum_i P_i \int \psi^{(i)*} \hat{L} \psi^{(i)} \, d^3 r_i, \tag{97.2}$$

where $\langle L \rangle$ denotes the mean value of the quantity in the mixed state, and $\overline{L}_i$ is its mean value in the ith pure state.

Let ψ_n be some complete set of orthonormalized functions, for instance, a set of eigenfunctions of an arbitrary Hermitian operator $\hat{M}$. Then, in the $\hat{M}$-representation for $\overline{L}_i$ we have the expression

$$\overline{L}_i = \sum_{n,\,m} a_n^{(i)*} a_m^{(i)} L_{nm},$$

where $a_n^{(i)}$ are the coefficients of expansion of $\psi^{(i)} = \sum_n a_n^{(i)} \psi_n$, and L_{nm} is the matrix elements of the operator $\hat{L}$, i.e. $L_{nm} = \int \psi_n^* \hat{L} \psi_m d^3r$. From this we find for $\langle L \rangle$

$$\langle L \rangle = \sum_{i,\,n,\,m} P_i a_n^{(i)*} a_m^{(i)} L_{nm}. \tag{97.3}$$

We introduce now the matrix $\hat{\rho}$ with elements ρ_{mn}:

$$\rho_{mn} = \sum_i P_i a_n^{(i)*} a_m^{(i)}, \tag{97.4}$$

which will be referred to as the *density matrix*. Then, the expression (97.3) for $\langle L \rangle$ acquires the form

$$\langle L \rangle = \sum_{n,\,m} \rho_{mn} L_{nm} = \sum_m (\hat{\rho}\hat{L})_{mm} = \mathrm{Tr}\,(\hat{\rho}\hat{L}). \tag{97.5}$$

Thus, knowing the density matrix, one can find the mean value of any physical quantity; therefore, the density matrix characterizes mixed states completely.

The elements of the density matrix obey definite relationships. From definition (97.4) follows that the matrix $\hat{\rho}$ is Hermitian:

$$\rho_{nm} = \rho_{mn}^*. \tag{97.6}$$

Furthermore, selecting for the operator $\hat{L}$ the unit operator $L_{nm} = \delta_{nm}$, we must obtain the mean value equal to unity, whence it follows that

$$\mathrm{Tr}\,\hat{\rho} = 1. \tag{97.7}$$

This condition has a simple physical meaning. The quantity $\rho_{nn} = \sum_i P_i \mid a_n^{(i)} \mid^2$ gives the probability of finding the subsystem in the state with wave function ψ_n. Therefore $\sum_n \rho_{nn} = \mathrm{Tr}\,\hat{\rho}$ is the probability of finding the subsystem in some state of the complete set ψ_n.

It should be noted that the trace of the matrix is invariant to unitary transformations and, therefore, the condition (97.7) and formula (97.5) remain the same in any representation. The number

of rows and columns of the density matrix depends on the number of independent states ψ_n used to characterize the pure state. For a system of spin moments $s = 1/2$, for instance, only two states are possible with different values of spin projections on the chosen direction $\psi_\uparrow$ and $\psi_\downarrow$, and the density matrix is of the two-row kind.

It should also be noted that a description by means of the density matrix is also possible when the system under consideration is isolated from the surroundings and is in a pure state. Furthermore, when one speaks of a macroscopic system, no information on the wave function of the pure state can be gained, since it is practically impossible to measure the complete set of quantities describing the state of the system. In addition, there is no need in it, since we are interested in the macroscopic state of the system which is characterized by mean values. But the knowledge of the density matrix requires much less information and, on the other hand, it provides an adequate thermodynamic description of the behaviour of a macroscopic system in terms of mean values.

Let us point to the presence of a simple criterion, permitting one to judge by the density matrix whether the state of a system is pure or mixed. In the case of a pure state $P_l = \delta_{lk}$, and, consequently, from formula (97.4) we find $\rho_{mn} = a_n^* a_m$, whence

$$(\rho^2)_{mn} = \sum_l \rho_{ml}\rho_{ln} = \sum_l a_l^* a_m a_n^* a_l = a_n^* a_m = \rho_{mn}, \quad \text{or} \quad \hat{\rho}^2 = \rho.$$

But no such relationship exists in the case of a mixed state.

Let us derive the equation of motion for a density matrix in the absence of interaction with the surroundings. According to formula (97.4), we have

$$\frac{\partial \rho_{mn}}{\partial t} = \sum_i P_i \left[\frac{\partial a_n^{(i)*}}{\partial t} a_m^{(i)} + a_n^{(i)*} \frac{\partial a_m^{(i)}}{\partial t} \right]. \tag{97.8}$$

From the expansion $\psi^{(i)} = \sum_n a_n^{(i)} \psi_n$ and Schrödinger's equation $i\hbar\, \partial\psi^{(i)}/\partial t = \hat{H}\psi^{(i)}$, we find

$$i\hbar \frac{\partial a_n^{(i)}}{\partial t} = \sum_i H_{nl} a_l^{(i)},$$

where H_{nl} is the matrix element of subsystem's Hamiltonian with no account taken of interaction with the surroundings, $H_{nl} = \int \psi_n^* H \psi_l d^3r$. Substituting Eq. (97.9) into Eq. (97.8), we obtain

$$i\hbar \frac{\partial \rho_{mn}}{\partial t} = H_{ml}\rho_{ln} - H_{nl}^* \rho_{ml} = H_{ml}\rho_{ln} - \rho_{ml}H_{ln} = (H\rho - \rho H)_{mn} \tag{97.9}$$

(we use the hermiticity of operator $\hat{H}$). It follows that the time variation of the density matrix $\hat{\rho}$ is described by the equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = [\hat{H}, \hat{\rho}]. \tag{97.10}$$

Thus, in the case of a steady-state closed system the density matrix commutes with the Hamiltonian of this system.

In the sections devoted to the kinetics of the phenomena in dense gases, we found that the kinetic equations describing the variation of distribution functions can be derived only in some limiting cases, not covering the great variety of possible physical conditions. Kubo proposed a solution method for problems in kinetics not involving the kinetic equations, which is associated with a direct application of the equation for the density matrix.

Let us solve the problem of the variation of the density matrix of a macroscopic system under the action of an external disturbing field. Let the system's Hamiltonian be equal to $\hat{H} + \hat{\mathcal{V}}$, where $\hat{\mathcal{V}}$ is the external field which will be considered below as a perturbation. The action of the surroundings manifests itself in that the system, left to itself (the external field is switched off), relaxates, approaching equilibrium with an equilibrium density matrix $\hat{\rho}_0$ ($[\hat{\rho}_0, \hat{H}] = 0$) and a characteristic relaxation time τ.

We write equation for the density matrix in the form

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} + [\hat{\rho}, \hat{H} + \hat{\mathcal{V}}] + \frac{i\hbar(\rho - \rho_0)}{\tau} = 0, \tag{97.11}$$

where the last term describes the process of relaxation resulting from the interaction with the surroundings. At the end of the analysis we shall eliminate this term, assuming that τ tends to infinity, and consider the system to be isolated again. Thus, the introduction of the term $i\hbar(\hat{\rho} - \hat{\rho}_0)/\tau$ acquires the meaning of a formal technique ensuring the convergence of the integrals involved in the theory on the intermediate stages.

Let us transform Eq. (97.11) into an integral equation, introducing the concept of the Heisenberg representation. The Heisenberg representation of operator $\hat{A}$ is the operator $\hat{\tilde{A}}$ specified by the formula

$$\hat{\tilde{A}} = e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}. \tag{97.12}$$

It is clear that the reciprocal relation also holds,

$$\hat{A} = e^{-i\hat{H}t/\hbar}\hat{\tilde{A}}e^{i\hat{H}t/\hbar} \tag{97.13}$$

It should be noted that if $\hat{A}$ commutes with the Hamiltonian $\hat{H}$, then $\tilde{\hat{A}} = \hat{A}$. For the density matrix we have

$$\hat{\rho} = e^{-i\hat{H}t/\hbar}\tilde{\hat{\rho}}e^{i\hat{H}t/\hbar}, \quad i\hbar\frac{\partial\hat{\rho}}{\partial t} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} + i\hbar e^{-i\hat{H}t/\hbar}\frac{\partial\tilde{\hat{\rho}}}{\partial t}e^{i\hat{H}t/\hbar}$$

and, substituting it into Eq. (97.11), we obtain

$$\frac{\partial\tilde{\hat{\rho}}}{\partial t} + \frac{\tilde{\hat{\rho}} - \tilde{\hat{\rho}}_0}{\tau} + \widetilde{\frac{[\hat{\rho}, \hat{\mathcal{U}}]}{i\hbar}} = 0.$$

Since the equilibrium density matrix is independent of time, this equation can be rewritten in the form

$$\frac{\partial(\tilde{\hat{\rho}} - \tilde{\hat{\rho}}_0)}{\partial t} + \frac{\tilde{\hat{\rho}} - \tilde{\hat{\rho}}_0}{\tau} = \frac{i}{\hbar}\widetilde{[\hat{\rho}, \hat{\mathcal{U}}]}. \tag{97.14}$$

Let us consider formally the right-hand side of Eq. (97.14) as an inhomogeneity. Then, the solution of the first-order equation for $\tilde{\hat{\rho}} - \tilde{\hat{\rho}}_0$, satisfying the initial condition $\tilde{\hat{\rho}} = \tilde{\hat{\rho}}_0$ at $t \to -\infty$, has the form

$$\tilde{\hat{\rho}} - \tilde{\hat{\rho}}_0 = \frac{i}{\hbar}e^{-t/\tau}\int_{-\infty}^{t} e^{\xi/\tau}\widetilde{[\hat{\rho}(\xi), \hat{\mathcal{U}}(\xi)]}\,d\xi. \tag{97.15}$$

Returning with the aid of relation (97.13) from Heisenberg's representations to the operators $\hat{\rho}$ and $\hat{\rho}_0$, we obtain

$$\hat{\rho} - \hat{\rho}_0 = \frac{i}{\hbar}e^{-t/\tau}\int_{-\infty}^{t} e^{\xi/\tau}e^{i\hat{H}(\xi-t)/\hbar}[\hat{\rho}(\xi), \hat{\mathcal{U}}(\xi)]\,e^{-i\hat{H}(\xi-t)/\hbar}\,d\xi. \tag{97.16}$$

Passing from ξ to the variable $\eta = t - \xi$, we have

$$\hat{\rho}(t) = \hat{\rho}_0 + \frac{i}{\hbar}\int_0^{\infty} e^{-\eta/\tau}e^{-i\hat{H}\eta/\hbar}[\hat{\rho}(t-\eta), \hat{\mathcal{U}}(t-\eta)]\,e^{i\hat{H}\eta/\hbar}\,d\eta. \tag{97.17}$$

Thus, we have found the integral equation for the density matrix $\hat{\rho}(t)$. Solving it by means of the iterative method and limiting ourselves to the first approximation, we obtain for the first-order addition to the density matrix

$$\hat{\rho}_1(t) = \frac{i}{\hbar}\int_0^{\infty} e^{-\eta/\tau}e^{-i\hat{H}\eta/\hbar}[\hat{\rho}_0, \hat{\mathcal{U}}(t-\eta)]\,e^{i\hat{H}\eta/\hbar}\,d\eta. \tag{97.18}$$

The above relationship is called the *Kubo formula*.

To illustrate the application of Kubo's formula, let us consider by way of example the problem of finding the conductivity tensor of a substance. Let the perturbation be a uniform electric field,

varying in time according to a harmonic law:

$$\mathcal{H}(t) = -\sum_j q\mathscr{E}\mathbf{r}^{(j)}e^{i\omega t} = -\sum_j q\mathscr{E}_\alpha x_\alpha^{(j)}e^{i\omega t}$$

(the indices $\alpha = 1, 2, 3$ imply summation, j is a particle's number). Then according to Eq. (97.18) we have

$$\rho_1(t) = -\frac{iq}{\hbar}e^{i\omega t}\mathscr{E}_\alpha\int_0^\infty e^{-\eta/\tau}e^{-i\hat{H}\eta/\hbar}\sum_j[\hat{\rho}_0,\ \hat{x}_\alpha^{(j)}]\,e^{-i\omega\eta+i\hat{H}\eta/\hbar}\,d\eta. \quad (97.19)$$

Let us find the mean value of the vector of current density in a system of charged particles with charge q and mass m:

$$\langle j_\alpha\rangle = \sum_j q\langle v_\alpha^{(j)}\rangle = \frac{q}{m}\sum_j\langle p_\alpha^{(j)}\rangle = \frac{q}{m}\sum_j \mathrm{Tr}\,(\hat{\rho}\hat{p}_\alpha^{(j)}) = \frac{q}{m}\sum_j \mathrm{Tr}\,(\hat{\rho}_1\hat{p}_\alpha^{(j)}).$$

We made use of formula (97.5) and also of the fact that there is no current in the equilibrium state in the absence of the field: $\sum_j \mathrm{Tr}\,(\hat{\rho}_0\hat{p}_\alpha^{(j)}) = 0$. According to formula (97.19), we find

$$\langle j_\alpha\rangle = \sigma_{\alpha\beta}\mathscr{E}_\beta e^{i\omega t},$$

where the conductivity tensor $\sigma_{\alpha\beta}$ is equal to

$$\sigma_{\alpha\beta} = \frac{q^2}{im\hbar}\int_0^\infty e^{-i\omega\eta-\eta/\tau}\sum_{k,\,j}\mathrm{Tr}\,\{\hat{\tilde{p}}_\alpha^{(k)}[\hat{\rho}_0,\ e^{-i\hat{H}\eta/\hbar}\hat{x}_\beta^{(j)}e^{i\hat{H}\eta/\hbar}]\}\,d\eta.$$

From the above formula we find the equivalent expression for $\sigma_{\alpha\beta}$,

$$\sigma_{\alpha\beta} = \frac{q^2}{im\hbar}\int_0^\infty e^{-i\omega\eta-\eta/\tau}\sum_{k,\,j}\mathrm{Tr}\,\{\hat{\tilde{p}}_\alpha^{(k)}[\hat{\rho}_0,\ \hat{x}_\beta^{(j)}]\}\,d\eta,$$

which is based on the possible cyclic permutation of operators under the sign Tr and on the commutativity of operators $\hat{\rho}_0$ and $\hat{H}$. It can, finally, happen to be convenient to carry out the transformation

$$\mathrm{Tr}\,\{\hat{\tilde{p}}_\alpha^{(k)}\hat{\rho}_0\hat{x}_\beta^{(j)} - \hat{\tilde{p}}_\alpha^{(k)}\hat{x}_\beta^{(j)}\hat{\rho}_0\} = \mathrm{Tr}\,(\hat{x}_\beta^{(j)}\hat{\tilde{p}}_\alpha^{(k)}\hat{\rho}_0 - \hat{\tilde{p}}_\alpha^{(k)}\hat{x}_\beta^{(j)}\hat{\rho}_0)$$
$$= \mathrm{Tr}\,\{[\hat{x}_\beta^{(j)}, \hat{\tilde{p}}_\alpha^{(k)}]\,\hat{\rho}_0\},$$

and the conductivity tensor can also be written in the form

$$\sigma_{\alpha\beta} = \frac{q^2}{im\hbar}\int_0^\infty e^{-i\omega\eta-\eta/\tau}\sum_{k,\,j}\mathrm{Tr}\,\{[\hat{x}_\beta^{(j)}, \hat{\tilde{p}}_\alpha^{(k)}]\,\hat{\rho}_0\}\,d\eta.$$

In the simplest case of a gas of non-interacting particles

$$\hat{H} = \sum_j \frac{\hat{p}^{(j)2}}{2m}, \quad \tilde{\hat{p}}_\alpha^{(k)} = \hat{p}_\alpha^{(k)}.$$

Then, accounting for $[\hat{x}_\beta^{(j)}, \hat{p}_\alpha^{(k)}] = i\hbar\,\delta_{\alpha\beta}\delta_{kj}$, we find for the conductivity tensor the isotropic expression

$$\sigma_{\alpha\beta} = \frac{nq^2}{m}\,\delta_{\alpha\beta}\int_0^\infty e^{-i\omega\eta-\eta/\tau}\,d\eta = \frac{nq^2}{m\left(i\omega+\frac{1}{\tau}\right)}\,\delta_{\alpha\beta}$$

(n is the number of electrons per unit volume). Assuming $\tau \to \infty$, we find

$$\sigma_{\alpha\beta} = \sigma\delta_{\alpha\beta}, \quad \sigma = \frac{nq^2}{i\omega m}.$$

Since conductivity is pertinent together with the dielectric permeability in the complex dielectric permeability in the combination $\varepsilon + 4\pi\sigma/i\omega$ this results in that the contribution of electrons to the dielectric permeability is equal to

$$\Delta\varepsilon = -\frac{4\pi nq^2}{m\omega^2}.$$

CHAPTER X

ELEMENTS OF NON-EQUILIBRIUM THERMODYNAMICS

In the concluding sections of the book, non-equilibrium states will be considered from the phenomenological viewpoint, resorting now and again to microscopic reasonings. The non-equilibrium thermodynamics, resulting from such an approach, has gained during the last years considerable progress that can be reflected in this book only to a small extent (see [49], [50]).

98. Balance Equations for Mass, Momentum, Energy and Entropy

In this section we shall generalize the equations derived in Sec. 94 and determining the variations of mass, momentum, energy and entropy (balance equations). These equations will be generalized in two respects.

The balance equation for the additive physical quantity A, having density ρa, where a is equal to A reduced to unit mass, takes the form

$$\frac{\partial}{\partial t}(\rho a) = -\nabla \mathbf{J}_a' + \sigma_a. \tag{98.1}$$

The quantity A can be a scalar or a vector- or a tensor component, and the vector $\mathbf{J}_a'$ represents the flux density of A. Upon integration of Eq. (98.1) over the volume and application of the Gauss theorem, the term $-\nabla \mathbf{J}_a'$ becomes the surface integral $-\oint\oint \mathbf{J}_a' d\sigma$, specifying the "amount" of the quantity A, leaving or entering in unit time the selected fixed volume, and σ_a represents the density of the source of quantity A, with $\int\int\int \sigma_a d^3r$ being equal to the amount of A that originated or vanished in volume V per unit time. It should be strongly emphasized that in the general case the flux $\mathbf{J}_a'$ is not reduced to the convective flux $\rho a \mathbf{u}$, i.e. to the transport of the quantity A with the flux of a substance, but that it contains, as it will be seen below, terms of another nature (a diffusion flow, heat flux, viscous flow, etc.).

For this reason Eq. (98.1) will be presented below in the form

$$\frac{\partial}{\partial t}(\rho a) = -\nabla(\rho a \mathbf{u} + \mathbf{J}_a) + \sigma_a, \tag{98.2}$$

assuming $\mathbf{J}_a$ to be the non-convective part of the flux. It is clear that the division of the right-hand side of (98.2) into a flux and source

is ambiguous: the term $-\nabla \mathbf{J}_\alpha$ or a part of it can be included either into the flux or source density σ_α. Therefore the balance equation (98.2) must in each concrete case take a form based on supplementary physical considerations.

Alongside with presenting the balance equation for quantity A in the form (98.2), we shall use another, substantional form of this equation. For this purpose let us introduce alongside with the local derivative with respect to time, $\partial/\partial t$, the substantial (total) derivative with respect to time

$$\frac{d}{dt} = \frac{\partial}{\partial t} + u_k \frac{\partial}{\partial x_k} = \frac{\partial}{\partial t} + \mathbf{u}\nabla. \tag{98.3}$$

Using formula (98.3) and the continuity equation $\partial\rho/\partial t = -\nabla\rho\mathbf{u}$, we write the balance equation in the form

$$\rho \frac{da}{dt} = -\nabla \mathbf{J}_\alpha + \sigma_\alpha. \tag{98.4}$$

Below, the balance equations for specific physical quantities (mass, momentum, energy, etc.) will be written in two forms, (98.2) and (98.4).

The second generalization of balance equations to be introduced here consists in that the gas will be assumed to consist of m chemical components with partial densities ρ_α, $\rho = \sum_\alpha \rho_\alpha$ being the total density of the gas. The mixture components will be assumed to participate in R chemical reactions with stoichiometric coefficients (see Sec. 31) $\nu_\alpha^{(j)}$ ($j = 1, 2, \ldots, R$; $\alpha = 1, 2, \ldots, m$). These reactions, as in Sec. 31, will be presented in the form $\sum_{\alpha=1}^{m} \nu_\alpha^{(j)} A_\alpha = 0$. Since the mass is conserved in each reaction, the following equation is valid

$$\sum_{\alpha=1}^{m} \nu_\alpha^{(j)} M_\alpha = 0, \tag{98.5}$$

where M_α is the molar mass of the αth component. We shall obtain the continuity equation for density ρ_α by introducing into Eq. (94.14) a term describing the change in mass due to the reaction,

$$\frac{\partial \rho_\alpha}{\partial t} = -\nabla(\rho_\alpha \mathbf{u}_\alpha) + \sum_{j=1}^{R} \nu_\alpha^{(j)} M_\alpha J_j, \tag{98.6}$$

where J_j is the rate of the jth reaction, i.e. the number of reaction acts reduced to unit volume and unit time and $\mathbf{u}_\alpha$ is the local (mean) velocity of the αth component.

Let us introduce the local centre-of-mass velocity $\mathbf{u} = \sum_{\alpha=1}^{m} \rho_\alpha \mathbf{u}_\alpha/\rho$ and the local diffusion rates for each component $\mathbf{w}_\alpha = \mathbf{u}_\alpha - \mathbf{u}$,

and also diffusion fluxes $\mathbf{I}_\alpha = \rho_\alpha \mathbf{w}_\alpha$, satisfying the condition $\sum_{\alpha=1}^{m} \mathbf{I}_\alpha = 0$. Performing in Eqs. (98.6) summation over all components, we obtain, in accordance with Eq. (98.5), the ordinary continuity equation $\partial\rho/\partial t = -\nabla(\rho\mathbf{u})$ for the total density.

Thus, for densities ρ and ρ_α there exist only convective fluxes $\rho\mathbf{u}$ and $\rho_\alpha \mathbf{u}_\alpha$. Sources exist only for partial densities $\sigma_{M_\alpha} = \sum_{j=1}^{R} \nu_\alpha^{(j)} M_\alpha J_j$, and the source of total density σ_M is equal to zero.

Passing with the aid of Eq. (98.3) to the total derivative with respect to time, we can readily present Eq. (98.6) in the substantial form:

$$\frac{d\rho_\alpha}{dt} = -\rho_\alpha \nabla \mathbf{u} - \nabla \mathbf{I}_\alpha + \sum_{j=1}^{R} \nu_\alpha^{(j)} M_\alpha J_j. \qquad (98.7)$$

Let us consider now Eq. (94.15) describing the variation of the total momentum of unit volume $\rho\mathbf{u}$. If the variations of the partial momenta of components is of no interest to us, the only change to be made in this equation consists in replacing F_i by $\sum_{\alpha=1}^{m} \rho_\alpha F_{\alpha i}$, where $F_{\alpha i}$ is the force acting upon unit mass of the αth component. We obtain

$$\frac{\partial}{\partial t}(\rho u_i) = -\frac{\partial}{\partial x_k}(\rho u_i u_k + P\delta_{ik} - \Pi_{ik}) + \sum_{\alpha=1}^{m} \rho_\alpha F_{\alpha i}. \qquad (98.8)$$

A natural interpretation of relationship (98.8) consists in that, in addition to the convective momentum flux with projections $\rho u_i u_k$, there exists a "viscous" momentum flux $P\delta_{ik} - \Pi_{ik}$, associated not with ordered gas flow (convection) but with random thermal motion. This motion also leads to inflow and outflow of momentum through the boundary of volume V and is characterized by the values of the tensor $P\delta_{ik} - \Pi_{ik}$ on the boundary of volume V. The source of total momentum is the total external force $\sum_{\alpha=1}^{m} \rho_\alpha \mathbf{F}_\alpha$.

Using relationship (98.4), we write the balance equation for momentum in the substantial form:

$$\rho \frac{du_i}{dt} = \frac{\partial}{\partial x_k}(P\delta_{ik} - \Pi_{ik}) + \sum_{\alpha=1}^{m} \rho_\alpha F_{\alpha i}. \qquad (98.9)$$

The balance equation (94.35) for kinetic energy will be written in a somewhat modified form:

$$\frac{\partial}{\partial t}\left(\frac{\rho u^2}{2}\right) = -\frac{\partial}{\partial x_k}\left[\frac{\rho u^2 u_k}{2} + (P\delta_{ik} - \Pi_{ik})\, u_i\right] + (P\delta_{ik} - \Pi_{ik})\frac{\partial u_i}{\partial x_k} + \sum_{\alpha=1}^{m} \rho_\alpha \mathbf{F}_\alpha \mathbf{u}. \quad (98.10)$$

This form of the balance equation for kinetic energy is based on the physical hypothesis that in addition to the convective flux $\rho u^2\mathbf{u}/2$, there exists at the boundary of the volume a "viscous" flux of kinetic energy with projections $(P\delta_{ik} - \Pi_{ik})\, u_i$, and the sources of kinetic energy, in addition to the work of external forces $\sum_\alpha \rho_\alpha \mathbf{F}_\alpha \mathbf{u}$, are represented by the work of forces of pressure and viscous friction [the second term on right-hand side of Eq. (98.10)]. The substantial form of Eq. (98.10) is

$$\rho \frac{d}{dt}\left(\frac{u^2}{2}\right) = -\frac{\partial}{\partial x_k}\left[(P\delta_{ik} - \Pi_{ik})\, u_i\right] + (P\delta_{ik} - \Pi_{ik})\frac{\partial u_i}{\partial x_k} + \sum_{\alpha=1}^{m} \rho_\alpha \mathbf{F}_\alpha \mathbf{u}. \quad (98.11)$$

The balance equation for potential energy undergoes still greater changes. According to the formula $\rho\psi = \sum_\alpha \rho_\alpha \psi_\alpha$ (ψ_α is the potential energy of the αth component, reduced to unit mass) and using Eq. (98.6), we have

$$\frac{\partial}{\partial t}(\rho\psi) = \sum_{\alpha=1}^{m} \psi_\alpha \frac{\partial \rho_\alpha}{\partial t} = -\sum_{\alpha=1}^{m} \psi_\alpha \frac{\partial}{\partial x_i}(\rho_\alpha u_{\alpha i}) + \sum_{j,\alpha} \nu_\alpha^{(j)} \psi_\alpha M_\alpha J_j. \quad (98.12)$$

In cases of practical interest, the last term of Eq. (98.12) vanishes, since the term $\sum_\alpha \nu_\alpha^{(j)} \psi_\alpha M_\alpha = 0$ — in chemical reactions mass, charge and other parameters on which potential energy may depend are conserved. Using formula $F_{\alpha i} = -\partial\psi_\alpha/\partial x_i$ and singling out the convective flux $\rho\psi\mathbf{u}$, the first term of Eq. (98.12) can be transformed in the following manner:

$$\sum_{\alpha=1}^{m} \psi_\alpha \frac{\partial}{\partial x_i}(\rho_\alpha u_{\alpha i}) = \frac{\partial}{\partial x_i}\left(\sum_{\alpha=1}^{m} \psi_\alpha \rho_\alpha u_{\alpha i}\right) + \sum_{\alpha=1}^{m} \rho_\alpha F_{\alpha i} u_{\alpha i}$$

$$= \nabla\left(\rho\psi\mathbf{u} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha \psi_\alpha\right) + \sum_{\alpha=1}^{m} \rho_\alpha \mathbf{F}_\alpha \mathbf{u} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha \mathbf{F}_\alpha.$$

Then, Eq. (98.12) acquires the form

$$\frac{\partial}{\partial t}(\rho\psi) = -\nabla\left(\rho\psi\mathbf{u} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\psi_\alpha\right) - \sum_{\alpha=1}^{m} \rho_\alpha \mathbf{F}_\alpha\mathbf{u} - \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\mathbf{F}_\alpha. \qquad (98.13)$$

It follows from Eq. (98.13) that the flux of potential energy contains, in addition to the convective term $\rho\psi\mathbf{u}$, the diffusion flux $\sum_\alpha \mathbf{I}_\alpha\psi_\alpha$, and the density of the source of potential energy includes, in addition to the work of external forces on the centre of mass, $\sum_\alpha \rho_\alpha \mathbf{F}_\alpha\mathbf{u}$, the work due to diffusion $\sum_\alpha \mathbf{I}_\alpha\mathbf{F}_\alpha$.

The substantial form of Eq. (98.13) is as follows:

$$\rho\frac{d\psi}{dt} = -\nabla\left(\sum_{\alpha=1}^{m} \mathbf{I}_\alpha\psi_\alpha\right) - \sum_{\alpha=1}^{m} \rho_\alpha\mathbf{F}_\alpha\mathbf{u} - \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\mathbf{F}_\alpha. \qquad (98.14)$$

The balance equation for the total mechanical energy of unit volume, $\rho E = \rho\,(u^2/2 + \psi)$, is obtained, summing up Eqs. (98.10) and (98.13):

$$\frac{\partial}{\partial t}(\rho E) = -\frac{\partial}{\partial x_k}\left\{\left[(\rho E + P)\,\delta_{lk} - \Pi_{lk}\right]u_l + \sum_{\alpha=1}^{m} I_{\alpha k}\psi_\alpha\right\}$$

$$+ (P\delta_{lk} - \Pi_{lk})\frac{\partial u_l}{\partial x_k} - \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\mathbf{F}_\alpha, \qquad (98.15)$$

or in the substantial form

$$\rho\frac{dE}{dt} = -\frac{\partial}{\partial x_k}\left[(P\delta_{lk} - \Pi_{\ k})\,u_l + \sum_{\alpha=1}^{m} I_{\alpha k}\psi_\alpha\right]$$

$$+ (P\delta_{,k} - \Pi_{lk})\frac{\partial u_l}{\partial x_k} - \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\mathbf{F}_\alpha. \qquad (98.16)$$

Let us write now the balance equation for the density of internal energy $\rho\tilde{U}$, defining it as the third component of the total energy density:

$$\rho E_t = \rho\frac{u^2}{2} + \rho\psi + \rho\tilde{U} = \rho\,(E + \tilde{U}).$$

Since the total energy has no sources, the balance equation for E_t has the form

$$\frac{\partial}{\partial t}(\rho E_t) = -\nabla\,(\rho E_t\mathbf{u} + \mathbf{J}_{E_t}), \qquad (98.17)$$

where the non-convective flux $\mathbf{J}_{E_l}$ is equal to

$$\mathbf{J}_{E_l i} = (P\delta_{ik} - \Pi_{ik})\, u_k + \sum_{\alpha=1}^{m} \psi_\alpha I_{\alpha i} + L_i \qquad (98.18)$$

and consists of the "viscous" flux, diffusion flux of potential energy and thermal flux [the first, the second and the third term on the right-hand side of Eq. (98.18) respectively]. This expression can be regarded as a phenomenological definition of the thermal flux L_i. Subtracting Eq. (98.15) from (98.17) and allowing for Eq. (98.18), we obtain the balance equation for the internal energy:

$$\frac{\partial}{\partial t}(\rho\tilde{U}) = -\nabla(\rho\tilde{U}\mathbf{u} + \mathbf{L}) - (P\delta_{ik} - \Pi_{ik})\frac{\partial u_i}{\partial x_k} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha \mathbf{F}_\alpha. \qquad (98.19)$$

Thus, in addition to the convective flux of internal energy, $\rho\tilde{U}\mathbf{u}$, energy is transported in the form of heat — the thermal flux $\mathbf{L}$, and the density of internal energy sources contains, in addition to the work of viscous forces and pressure, the diffusion term $\sum_\alpha \mathbf{I}_\alpha \mathbf{F}_\alpha$. For a single-component gas this term in Eq. (98.19) vanishes and we return to Eq. (94.38). We have already mentioned that the division of the right-hand side of the balance equation into the "flux" and "source" is ambiguous. In particular, we could transform the second term on the right-hand side of Eq. (98.19) in the following manner:

$$-(P\delta_{ik} - \Pi_{ik})\frac{\partial u_i}{\partial x_k} = -\frac{\partial}{\partial x_k}[(P\delta_{ik} - \Pi_{ik})\, u_i] + u_i \frac{\partial}{\partial x_k}(P\delta_{ik} - \Pi_{ik})$$

and include the term $(P\delta_{ik} - \Pi_{ik})\, u_i$ into the non-convective flux. The reason for not doing it and writing the balance equation in the form of (98.19) is justified by the natural physical hypothesis, according to which the forces of viscous friction and pressure are responsible for the transport of mechanical energy of ordered gas flow, and not for the transport of energy of random thermal motion. The substantial form of Eq. (98.19) is as follows:

$$\rho\frac{d\tilde{U}}{dt} = -\nabla\mathbf{L} - (P\delta_{ik} - \Pi_{ik})\frac{\partial u_i}{\partial x_k} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha \mathbf{F}_\alpha. \qquad (98.20)$$

Let us turn, finally, to deriving the balance equation for entropy, following the assumption on the existence of local equilibrium, made in Sec. 94. According to this assumption, the local molar entropy is specified by the expression

$$d\tilde{S} = \frac{d\tilde{U} + P\, d\tilde{V} - \sum_{\alpha=1}^{m} \mu_\alpha\, dN_\alpha}{T}, \qquad (98.21)$$

where N_α is the molar fraction and μ_α is the chemical potential of the αth component.

Let us assume that the expression remains valid along the path of the centre of mass of a small volume of a gas. Multiplying both sides of Eq. (98.21) by ρ, replacing $\widetilde{V} = \rho^{-1}$ and passing to the substantial derivative with respect to time, we obtain

$$\rho \frac{d\widetilde{S}}{dt} = T^{-1}\left[\rho \frac{d\widetilde{U}}{dt} - P\rho^{-1}\frac{d\rho}{dt} - \rho \sum_{\alpha=1}^{m} \mu_\alpha \frac{dN_\alpha}{dt}\right]. \qquad (98.22)$$

Equation (98.22) can be transformed with the iad of formula (98.20), the substantial form of the continuity equation $d\rho/dt = -\rho\nabla\mathbf{u}$, the replacement $\rho_\alpha = \rho N_\alpha$ and relationship (98.7). Upon simple transformations we obtain

$$\rho \frac{d\widetilde{S}}{dt} = T^{-1}\left[-\nabla\mathbf{L} + \Pi_{lk}\frac{\partial u_l}{\partial x_k} + \sum_{\alpha=1}^{m} \mathbf{I}_\alpha \mathbf{F}_\alpha + \sum_{\alpha=1}^{m} \mu_\alpha \nabla \mathbf{I}_\alpha - \sum_{j=1}^{R} A_j J_j\right], \qquad (98.23)$$

where the quantity

$$A_j = \sum_{\alpha=1}^{m} \nu_\alpha^{(j)} M_\alpha \mu_\alpha \qquad (98.24)$$

is called the *chemical affinity* of the jth reaction. It is readily seen that the quantities A_j vanish in the state of thermodynamic equilibrium. Using formula (98.3), let us also transform Eq. (98.23) to the local form:

$$\frac{\partial}{\partial t}(\rho\widetilde{S}) = -\nabla\left(\rho\widetilde{S}\mathbf{u} + \frac{\mathbf{L} - \sum_{\alpha=1}^{m} \mu_\alpha \mathbf{I}_\alpha}{T}\right) + \mathbf{L}\nabla(T^{-1})$$

$$-T^{-1}\sum_{\alpha=1}^{m} \mathbf{I}_\alpha\left[T\nabla\left(\frac{\mu_\alpha}{T}\right) - \mathbf{F}_\alpha\right] + T^{-1}\Pi_{lk}\frac{\partial u_l}{\partial x_k} - T^{-1}\sum_{j=1}^{R} A_j J_j. \qquad (98.25)$$

The interpretation of Eq. (98.25) is clear: in addition to the convective entropy flux $\rho\widetilde{S}\mathbf{u}$, there exist the heat flux L/T and the diffusion flux $-\sum_\alpha \mu_\alpha \mathbf{I}_\alpha/T$, and the source strength of entropy sources is determined by the formula

$$\sigma_S = \mathbf{L}\nabla(T^{-1}) - \sum_{\alpha=1}^{m} \mathbf{I}_\alpha\left[\nabla\left(\frac{\mu_\alpha}{T}\right) - \frac{\mathbf{F}_\alpha}{T}\right] + T^{-1}\Pi_{lk}\frac{\partial u_l}{\partial x_k} - \sum_{j=1}^{R} \frac{A_j J_j}{T}, \qquad (98.26)$$

and, consequently, entropy generation in a gas is due to four irreversible processess—heat conductivity due to the presence of a temperature gradient [the term $\mathbf{L}\nabla(T^{-1})$], diffusion caused by the presence of both external forces and gradients of chemical potentials and temperature [the second term in formula (98.26)], viscosity due to the presence of velocity gradients (the term $T^{-1}\Pi_{ik}\partial u_i/\partial x_k$), and chemical reactions.

Expression (98.26) is bilinear: each term contains a flux-type factor (heat flux $\mathbf{L}$, diffusion flux $\mathbf{I}_\alpha$, momentum flux or viscosity tensor Π_{ik}, and rate of chemical reaction J_j) and the factor proportional to the gradient of some quantity, such as temperature, chemical potential, potential energy (force F_α), velocity. The chemical affinity in the last term of formula (98.26) is associated, according to (98.24), with the change in the chemical potential, and is, consequently, a quantity of the gradient type in the density space, ρ_α.

The first factors of the flux-type will be denoted below by symbols $Y^{(i)}$ and called *fluxes*, the second factors will be denoted by $X^{(i)}$ and called *thermodynamic forces* conjugate to the fluxes $Y^{(i)}$. The formula expressing the density of entropy sources will be usually referred to below as *entropy generation*, in accordance with the commonly used terminology; its general form is as follows:

$$\sigma_S = \sum_i Y^{(i)} X^{(i)}, \tag{98.27}$$

where summation is performed over all the irreversible processes occurring in the system.

The reader's attention should be drawn to the fact that the fluxes $Y^{(i)}$ and their conjugate thermodynamic forces $X^{(i)}$, associated with various non-equilibrium processes, can have different tensor dimensions. So for thermal conductivity $\mathbf{Y}^{(q)} = \mathbf{L}$ and $\mathbf{X}^{(q)} = \nabla(T^{-1})$ are vectors. For diffusion $\mathbf{Y}_\alpha^{(d)} = -\mathbf{I}_\alpha$ and $\mathbf{X}_\alpha^{(d)} = \nabla\left(\frac{\mu_\alpha}{T}\right) - \frac{F_\alpha}{T}$ are also vectors. In the case of chemical reactions we have $Y_j^{(ch)} = -A_j$ and $X_j^{(ch)} = J_j/T$ and the fluxes and forces are scalars. Finally, for viscous processes $Y_{ik}^{(v)} = \Pi_{ik}$ and $X_{ik}^{(v)} = \frac{1}{T}\frac{\partial u_i}{\partial x_k}$; the fluxes and forces are tensors of the second rank. Strictly speaking, the terms in Eq. (98.26) associated with viscosity should be divided into tensors and scalars, taking out from tensor Π_{ik} and tensor $\partial u_i/\partial x_k$ the zero-trace scalar terms due to bulk viscosity [Sec. 94, formula (94.20)]. We shall not consider here, however, this more complicated form of the theory (see [49]), assuming for the sake of simplicity the bulk viscosity η to be equal to zero. It is clear that by virtue of the invariance of σ_S with respect to rota

tions, the flux and its conjugate thermodynamic force must have the same tensor dimension, as was shown above.

Expression (98.27) is of a rather general nature: it is valid not only for fluids (liquids and gases) but also for the case of anisotropic crystals, when terms corresponding to viscosity are absent. On the other hand, in the presence of external fields expression (98.27) can contain, in addition to the four above-mentioned terms (thermal conductivity, diffusion, viscous friction and chemical reactions) the terms proportional to the field gradient. For instance, in a problem on electric conductivity the equation for σ_S will contain (see next section) a term, proportional to the product of current density and electric field intensity.

99. Small Deviations from Equilibrium Onsager's Principle

This section is devoted to irreversible processes with small deviations from equilibrium. Since in equilibrium both the fluxes $Y^{(i)}$ and the thermodynamic forces $X^{(i)}$ are equal to zero, it is natural to assume that close to equilibrium there exist the following linear relationships between fluxes and forces:

$$Y^{(i)} = \sum_k L_{ik} X^{(k)}. \tag{99.1}$$

The coefficients L_{ik} are called the *phenomenological* or *kinetic coefficients*, and relationships (99.1) are referred to as the *phenomenological equations*. The diagonal coefficients in Eq. (99.1) are called eigen coefficients, describing "ordinary" transport phenomena. We assume that matrix L_{ik} is diagonal, $L_{ik} = L_i \delta_{ik}$; then relation (99.1) takes the form $Y^{(i)} = L_i X^{(i)}$ and coincides with the known empirical laws of transport. The presence of the gradient $X^{(i)}$ in the system gives rise to the basic transport process and its characteristic flux $Y^{(i)}$ proportional to the gradient.

Thus, for instance, the presence of a temperature gradient gives rise to the main process of heat conductivity—the transfer of heat proportional to ∇T (Fourier's law), the existence of a density gradient causes diffusion—mass transfer proportional to $\nabla \rho$ (Fick's law), and electric field gradient (field intensity) gives rise to electric current—the transport of charge proportional to $\nabla \varphi = -\mathscr{E}$ (Ohm's law), etc.

Alongside with these "basic" transport processes, there exist, however, "auxiliary" processes linked inseparably with the "basic" ones. So, for instance, the transport of charge, induced by an electric field (the motion of ions in electrolyte or electrons in metal), may cause simultaneously both the transfer of their kinetic energy (heat)

and of mass (diffusion), with the two "conjugate" transport processes being also proportional to $\nabla\varphi$ in the first approximation. On the contrary, mass transfer owing to a density gradient or heat transfer caused by a temperature gradient can simultaneously cause, it we speak of a system of charged particles, charge transport, and the appearance of an electromotive force proportional to the density gradient $\nabla\rho$ and temperature gradient ∇T in the two cases. In the presence of temperature gradient heat transfer can be accompanied by mass transfer (thermal diffusion). Such "side" or "cross" processes are characterized by non-diagonal coefficients L_{ik}, referred to as phenomenological coefficients. A part of the coefficients L_{ik} can be identically equal to zero due to the symmetry properties of the system under consideration, meaning that in the general case the components of fluxes do not depend on all the components of the thermodynamic forces. This statement is called the *Curie symmetry principle.*

For an isotropic fluid system, in particular, in the absence of an external field, only fluxes and forces of the same tensor dimension can be linearly related to each other (see [51]). On the contrary, the phenomenological coefficients L_{ik}, relating a flux of one dimensionality to a thermodynamic force of another dimensionality, are identically equal to zero. Consequently, with an appropriate labeling of indices, the matrix L_{ik} is then quasi-diagonal, consisting of "blocks" relating scalar fluxes and scalar forces, vector fluxes and vector forces, etc.

In particular, in an isotropic system the scalar rates of chemical reactions can be functions only of chemical affinity (of all the reactions that are possible in the system). The thermal conductivities in various directions, forming the heat flux vector, can depend not only on the components of vector $\nabla(T^{-1})$, but also on the components of vectors $\nabla(\mu_\alpha/T)$, $\mathbf{F}_\alpha/T$, and in the presence of an electric field also on the components of $\nabla\varphi = -\mathscr{E}$ (thermoelectric phenomena). Similarly, the components of diffusion fluxes $\mathbf{I}_\alpha$ can depend, in addition to the components of the "eigen" thermodynamic force, on the components of the vector $\nabla(T^{-1})$ (thermal diffusion) and on the components of field intensity; the components of the current density vector, in addition to $\nabla\varphi$, depend in the general case on $\nabla(\mu_\alpha/T)$ (the electrochemical effect in electrolytes) and on $\nabla(T^{-1})$ (Thomson's effect). Allowing for Eq. (99.1), formula (98.27) for entropy production acquires the following form:

$$\sigma_S = \sum_{i,\,k} L_{ik} X^{(i)} X^{(k)}. \tag{99.2}$$

Production of entropy is a quadratic homogeneous function of thermodynamic forces. The condition that $\sigma_S \geqslant 0$ imposes some restrictions on the coefficients L_{ik}, known to consist in that the

diagonal coefficients should be non-negative

$$L_{ii} \geqslant 0, \tag{99.3}$$

and the non-diagonal coefficients should satisfy the inequalities

$$L_{ii}L_{kk} \geqslant \frac{1}{4}(L_{ik} + L_{ki})^2. \tag{99.4}$$

Due to the fact that matrix L_{ik} is quasi-diagonal, expression (99.2) for entropy production is represented as the sum of independent terms corresponding to scalar, vector and tensor forces, and the condition that σ_S should be non-negative can be written for each of the terms separately.

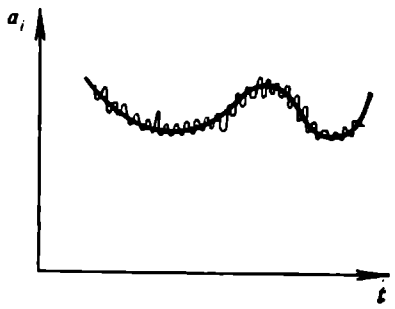

FIG. 117

Let us prove now the important property of the coefficients L_{ik}, referred to as the *Onsager reciprocal relations*, consisting in that the matrix of the coefficients L_{ik} is symmetric, $L_{ik} = L_{ki}$ (with some reservations that will be formulated below). The ideas of phenomenological thermodynamics are no longer sufficient to prove the Onsager relations, and use should be made of the microscopic theory. The basic hypothesis on which Onsager's theory is based consists in that a macroscopic weakly non-equilibrium state of a system can be considered with the aid of the methods of statistical physics, assuming the state to be a strong fluctuation. In other words, according to Onsager's hypothesis, the gradients of temperature, density, Cartesian velocity components, etc., created in non-equilibrium macroscopic system by external disturbances, obey the same statistical laws as the gradients due to fluctuations.

Let us characterize a closed system by a set of parameters a_i equal to zero in equilibrium. It should be stressed that the parameters a_i fail to be actually microscopic quantities, but are "semimicroscopic" or "semimacroscopic", meaning that they represent the values of some microscopic parameters averaged over weak frequent fluctuations (the thin curve in Fig. 117), and their variation in time characterizes the behaviour of strong fluctuations (the solid line in Fig. 117). Since in equilibrium the entropy of the system assumes its maximum value, then close to equilibrium we have the equality

$$\Delta S = -\sum_{i,k} \beta_{ik} a_i a_k, \tag{99.5}$$

where the non-negative definite matrix β_{ik} can be chosen symmetric, $\beta_{ik} = \beta_{ki}$. On the other hand, near the equilibrium state the rate

of variation of parameters $\dot{a}_i$ must also be a small quantity, since in equilibrium $\dot{a}_i$ take constant (zero) values and vanish.

Let us assume that near equilibrium the velocities $\dot{a}_i$ are the first-order infinitesimals in $\dot{a}_i$:

$$\dot{a}_l = -\sum_k \alpha_{lk} a_k. \tag{99.6}$$

Assuming entropy to be a function of parameters a_i, we find for the time derivative dS/dt, which for a closed system coincides with the entropy source density (production of entropy) σ_S, the expression

$$\sigma_S = \frac{dS}{dt} = \sum_i \dot{a}_l \frac{\partial S}{\partial a_l}. \tag{99.7}$$

The further proof is based on the fact that the first factor on the right-hand side of Eq. (99.7) is identified with the flux, and the second with its conjugate thermodynamic force:

$$Y^{(i)} = \dot{a}_l, \quad X^{(i)} = \frac{\partial S}{\partial a_l}. \tag{99.8}$$

It is actually not always possible to define the flux as a time derivative of the quantity a_l. It can, however, be shown [50] that the property of the kinetic coefficients L_{ik} which we prove here is also true in the case of other definitions of fluxes and thermodynamic forces, i.e. one can always pass from one system of fluxes and forces $Y^{(i)}$, $X^{(i)}$ to another system $\tilde{Y}^{(i)}$ and $\tilde{X}^{(i)}$, keeping the sum $\sum_i X^{(i)} Y^{(i)}$ invariant.

Let us find the relation between the fluxes and the forces. We find from relationships (99.5) and (99.8) that

$$X^{(i)} = \frac{\partial S}{\partial a_l} = \frac{\partial (\Delta S)}{\partial a_l} = -\sum_k \beta_{lk} a_k,$$

whence, introducing the reciprocal matrix β^{-1}_{jl}, we obtain $a_j = -\sum_l \beta^{-1}_{jl} X^{(l)}$. Substituting the expression into Eq. (99.6), we find

$$Y^{(i)} = \dot{a}_l = -\sum_j \alpha_{lj} a_j = \sum_{j,k} \alpha_{lj} \beta^{-1}_{jk} X^{(k)}$$

and, consequently, the expression for the kinetic coefficients L_{ik} is

$$L_{ik} = \sum_j \alpha_{lj} \beta^{-1}_{jk}.$$

Let us proceed from the equation

$$Y^{(i)} = \dot{a}_i = \sum_k L_{ik} X^{(k)} = \sum_k L_{ik} \frac{\partial S}{\partial a_k} \tag{99.9}$$

and to prove the symmetry of coefficients L_{ik}, consider the product $a_i(t)\, a_k(t+\tau)$, where τ is a time interval, small compared to the characteristic time for the change in a_k (the recurrence time for strong fluctuations). Then, we have with a sufficient degree of accuracy

$$a_k(t+\tau) = a_k(t) + \tau \dot{a}_k = a_k(t) + \tau \sum_l L_{kl} \frac{\partial S}{\partial a_l}. \tag{99.10}$$

The definition of $a_k(t)$ does not uniquely determine the state of the system at the instant of time $t+\tau$, since there exists, in addition, a number of parameters $a_l(t)$ $(l \neq k)$ and the more so it does not determine the value of $a_k(t+\tau)$, since with a given $a_k(t)$ a number of processes may occur, leading to different values of $a_k(t+\tau)$.

Let us find the mean value of the expression $a_i(t)\, a_k(t+\tau)$:

$$\overline{a_i(t)\, a_k(t+\tau)} = \overline{a_i(t)\, a_k(t)} + \tau \sum_l \overline{L_{kl} a_i(t) \frac{\partial S}{\partial a_l}}.$$

Let us use the expression for the probability density of fluctuations, $\rho = Ae^S$. This yields

$$\overline{a_i(t) \frac{\partial S}{\partial a_l}} = A \int a_i(t) \frac{\partial S}{\partial a_l} e^S d\Gamma = A \int a_i(t) \frac{\partial}{\partial a_l}(e^S)\, d\Gamma.$$

Let us integrate this expression by parts and make use of the fact that the probability Ae^S of deviation from equilibrium decreases very rapidly with increasing deviation, so that the term outside the integral can be assumed to equal zero. In consequence, we obtain

$$\overline{a_i(t) \frac{\partial S}{\partial a_l}} = -A \int e^S \frac{\partial a_i}{\partial a_l} d\Gamma = -\delta_{il},$$

since $\partial a_i / \partial a_l = \delta_{il}$ and $A \int e^S d\Gamma = 1$ by virtue of the normalization condition. Thus, we have

$$\overline{a_i(t)\, a_k(t+\tau)} = \overline{a_i(t)\, a_k(t)} - \tau L_{ki}.$$

Similarly, we can obtain the relationship

$$\overline{a_k(t)\, a_i(t+\tau)} = \overline{a_k(t)\, a_i(t)} - \tau L_{ik}.$$

If the parameters a_i, a_k are such that they do not change upon a change of the sign of all velocities, then owing to the symmetry

of equations of mechanics in respect to the time reflection operation, it makes no difference which of the quantities a_i, a_k we take at the earlier, and which at the next instant of time, and. consequently,

$$\overline{a_k(t)\,a_i(t+\tau)} = \overline{a_i(t)\,a_k(t+\tau)}.$$

From this it follows that

$$L_{ik} = L_{ki}. \tag{99.11}$$

Expression (99.11) is also true for the case when the two quantities a_i and a_k are proportional to the first (or, in general, odd) power of velocity and change the sign upon time reflection. But if in this case only one of the two quantities, a_i or a_k, changes sign then

$$L_{ik} = -L_{ki}. \tag{99.12}$$

Finally, it should be noted that in the presence of a magnetic field **H** the equations of motion are symmetric with respect to the change of the sign of time only in the case of a simultaneous change in the sign of magnetic field intensity **H**, and the symmetry principle for the kinetic coefficients is then written in the form

$$L_{ik}(\mathbf{H}) = \pm L_{ki}(-\mathbf{H}). \tag{99.13}$$

100. Corollaries of Onsager's Reciprocal Relations. Theorem on the Minimum Production of Entropy for Stationary States. Examples

An important particular case of non-equilibrium processes are steady-state processes in the course of which the boundary conditions imposed on a system prevent its approaching equilibrium. So, for example, due to external effects, a constant temperature difference, pressure drop, components concentrations, a constant potential difference, etc., can be maintained in the system.

In contrast to equilibrium states, in such stationary states the production of entropy does not vanish. It is, however, possible to prove an important theorem, stating that in stationary, weakly non-equilibrium states the total production of entropy is minimum.

We shall limit ourselves to an illustration of this theorem by considering simple examples. Let us consider as the first example a system at whose boundaries a constant temperature difference is maintained (viscous processes are assumed to be absent). Then, the phenomenological equation (99.1) reduces to

$$\mathbf{L} = L_{qq}\nabla(T^{-1}), \tag{100.1}$$

and formula (98.27) for entropy production takes the form

$$\sigma_S = \mathbf{L}\nabla(T^{-1}) = L_{qq}[\nabla(T^{-1})]^2. \tag{100.2}$$

The coefficient L_{qq} is related to the thermal conductivity $\varkappa$ by the obvious relationship $\varkappa = L_{qq}/T^2$, which follows from (100.1) and from the definition of thermal conductivity, $\mathbf{L} = -\varkappa\nabla T$, and for a weakly non-equilibrium system it can be assumed to be independent of coordinates.

The total production of entropy P_S is equal to the volume integral of the source density σ_S:

$$P_S = \int \sigma_S \, d^3r = L_{qq} \int d^3r \, |\nabla (T^{-1})|^2. \tag{100.3}$$

Let us find the conditions for the functional (100.3) to be minimum, assuming that temperatures on the boundaries are given and that the variations δT on the boundaries are equal to zero. The Euler equations for this extremum case have the following form:

$$\nabla^2 (T^{-1}) = L_{qq}^{-1} \nabla \mathbf{L} = 0.$$

Since, apart from it, the temperature satisfies the equation $\rho c \, \partial T/\partial t = -\nabla \mathbf{L}$, we arrive at the conclusion that the state with a minimum production of entropy is a stationary state, $\partial T/\partial t = 0$.

It can readily be shown that the stationary state is stable in respect to small temperature fluctuations. Differentiating expression (100.3) with respect to t and applying the Gauss theorem, we get

$$\frac{\partial P_S}{\partial t} = 2L_{qq} \int d^3r \nabla (T^{-1}) \frac{\partial}{\partial t} [\nabla (T^{-1})] = 2 \int d^3r \, \mathbf{L} \nabla \left[\frac{\partial}{\partial t} (T^{-1}) \right]$$

$$= 2 \oint d\sigma \mathbf{L} \frac{\partial}{\partial t} (T^{-1}) + 2 \int d^3r \frac{\nabla \mathbf{L} \frac{\partial T}{\partial t}}{T^2} = -2\rho c \int d^3r \frac{\left(\frac{\partial T}{\partial t} \right)^2}{T^2} \leqslant 0.$$

The surface integral, appearing when the Gauss theorem is applied by parts, is equal to zero, since the temperature at the walls is constant. Thus, with local temperature fluctuations, the production of entropy diminishes and tends to a minimum.

The second example to be considered involves a system in which there are two fluxes, $Y^{(1)}$ and $Y^{(2)}$, of equal tensor dimension and two thermodynamic forces, $X^{(1)}$ and $X^{(2)}$, conjugate to the fluxes.

The specific production of entropy is expressed by

$$\sigma_S = Y^{(1)} X^{(1)} + Y^{(2)} X^{(2)}, \tag{100.4}$$

and the phenomenological equations reduce to

$$Y^{(1)} = L_{11} X^{(1)} + L_{12} X^{(2)},$$

$$Y^{(2)} = L_{12} X^{(1)} + L_{22} X^{(2)}, \quad L_{21} = L_{12}. \tag{100.5}$$

Substituting Eq. (100.5) into Eq. (100.4), we obtain

$$\sigma_S = L_{11} X^{(1)2} + 2L_{12} X^{(1)} X^{(2)} + L_{22} X^{(2)2}. \tag{100.6}$$

Assuming $X^{(1)}$ to be constant and differentiating Eq. (100.6) with respect to $X^{(2)}$, we find

$$\frac{1}{2}\left(\frac{\partial\sigma_S}{\partial X^{(2)}}\right)_{X^{(1)}} = L_{12}X^{(1)} + L_{22}X^{(2)} = Y^{(2)} = 0 \qquad (100.7)$$

and, by analogy

$$\frac{1}{2}\left(\frac{\partial\sigma_S}{\partial X^{(1)}}\right)_{X^{(2)}} = L_{11}X^{(1)} + L_{12}X^{(2)} = Y^{(1)} = 0. \qquad (100.8)$$

When the determinant $L_{12}^2 - L_{11}L_{22}$ differs from zero, only the values $X^{(1)} = 0$, $X^{(2)} = 0$ satisfy Eqs. (100.7) and (100.8). This means that minimum entropy production, equal to zero, is attainable only in the equilibrium state, with the condition for the zero value of σ_S to be minimum or expression (100.6) to be non-negative suggesting, in addition, the fulfillment of the inequality $L_{12}^2 - L_{11}L_{12} \leqslant \leqslant 0$. However, if one of the thermodynamic forces, $X^{(2)}$, for instance, is fixed, the fact that σ_S is minimum is equivalent, as is seen from Eq. (100.8), to the zero flux $Y^{(1)} = a_1$, i.e. to the steady-state nature of the process.

Let us consider by way of example a system with two fluxes and two thermodynamic forces of the same (vectorial) dimension, namely, a non-equilibrium electron gas in an isotropic metal or semiconductor, in which there exists a temperature gradient and a time-independent electric field gradient $\nabla\varphi\,(x, y, z)$. In the presence of an external field the chemical potential of electrons is specified by the formula

$$\mu = \mu_0\,(T,\ n) - e\varphi\,(x,\ y,\ z) \qquad (100.9)$$

where $\mu_0\,(T, n)$ is the chemical potential in the absence of a field, which depends on temperature and density. According to formula (98.26), the specific entropy production σ_S is expressed by

$$\sigma_S = \mathbf{L}\nabla\,(T^{-1}) - \mathbf{I}\nabla\left(\frac{\mu}{T}\right). \qquad (100.10)$$

For our purposes it is, however, convenient to determine the heat flux $\mathbf{L}$ in another way, eliminating from it the term representing energy transport by the particles' flux. Let us denote the new flux $\tilde{\mathbf{L}} = \mathbf{L} - \mu\mathbf{I}$. Then, we obtain

$$\sigma_S = \tilde{\mathbf{L}}\nabla\,(T^{-1}) - \frac{I}{T}\nabla\mu, \qquad (100.11)$$

and the phenomenological relations acquire the form

$$\begin{aligned} \tilde{\mathbf{L}} &= L_{11}\nabla\,(T^{-1}) + L_{12}\frac{\nabla\mu}{T}, \\ -\mathbf{I} &= L_{21}\nabla\,(T^{-1}) + L_{22}\frac{\nabla\mu}{T}. \end{aligned} \qquad (100.12)$$

The Onsager relation $L_{21} = L_{12}$ can be shown to remain valid when passing to a new flux and thermodynamic force $\nabla\mu/T$. Relations (100.12) contain three independent coefficients that can be shown to be expressed in terms of measurable quantities, such as thermal conductivity $\varkappa$, electrical conductivity σ and differential thermoelectromotive force ε. Assuming in Eq. (100.12) $\mathbf{I} = 0$ and eliminating $\nabla\mu/T$, we get

$$\tilde{\mathbf{L}} = -\frac{L_{11}L_{22} - L_{12}^2}{L_{22}T^2}\nabla T,$$

whence we have

$$\varkappa = \frac{L_{11}L_{22} - L_{12}^2}{L_{22}T^2} \tag{100.13}$$

Due to the fact that L_{22} and $L_{11}L_{22} - L_{12}^2$ are positive, we obtain $\varkappa > 0$. Let there be no temperature (and density) gradient in the specimen. Allowing for Eq. (100.9), the second of Eqs. (100.12) yields

$$\mathbf{j} = -e\mathbf{I} = \frac{eL_{22}}{T}\nabla\mu = -\frac{e^2L_{22}}{T}\nabla\varphi = \frac{e^2L_{22}}{T}\mathscr{E},$$

whence we find for the electrical conductivity the expression

$$\sigma = e^2L_{22}/T. \tag{100.14}$$

Finally, at $\mathbf{I} = 0$, we find from Eq. (100.12)

$$\varepsilon = \frac{\nabla\mu}{e} = \frac{L_{21}}{L_{22}eT}\nabla T.$$

The quantity ε, equal to $\nabla\mu_0/e - \nabla\varphi = \mathscr{E} + \mathscr{E}_{ext}$, represents the sum of the electric field intensity $\mathscr{E}$ and the intensity of the external force field $\mathscr{E}_{ext} = -\nabla\mu_0/e$ and, consequently, gives the electromotive force per unit length—the differential thermoelectromotive force due to the temperature gradient (the thermoelectric effect).

At $\nabla\varphi = 0$, $\tilde{\mathbf{L}}$ and $\mathbf{j}$ are defined by the expressions

$$\tilde{\mathbf{L}} = \frac{L_{12}}{T}\nabla\mu_0, \quad \mathbf{j} = \frac{eL_{22}}{T}\nabla\mu_0. \tag{100.15}$$

Due to the fact that temperature is constant we have

$$\nabla\mu_0 = \tilde{V}\nabla P = \frac{N_A}{n}\nabla P.$$

If the gas of current carriers can be assumed to be ideal, then $\nabla P = T\nabla n$, and relations (100.15) reduce to

$$\tilde{\mathbf{L}} = \frac{L_{12}N_A}{n}\nabla n, \quad \mathbf{j} = \frac{L_{22}N_Ae}{n}\nabla n.$$

The direction of the electric current (referred to as diffusion current) coincides with that in which the concentration of current carriers decrease, and the direction of the heat flux is not determined and it depends on the sign of L_{12}.

Problems

1. Consider the contact between two conductors (semiconductors) A and B, replacing in formulae (100.12) the gradients ∇T and $\nabla\mu$ by the differences ΔT and $\Delta\mu$. Derive the expression for the Peltier heat liberated in the contact at $\Delta T = 0$.

Answer. $\Delta Q = | \tilde{\mathbf{L}}_A - \tilde{\mathbf{L}}_B | = \Pi_{AB} I$, where $\Pi_{AB} = e^{-1}\left(\frac{L_{12}^{(A)}}{L_{22}^{(A)}} - \frac{L_{12}^{(B)}}{L_{22}^{(B)}}\right)$ is the Peltier coefficient.

2. Prove the formula relating the Peltier coefficient and the thermoelectromotive force in the junction: $\varepsilon_{AB} = -\Pi_{AB}/T$ (Thomson's second relation).

101. Far-From-Equilibrium States

This concluding section is devoted to states of a macroscopi system far from thermodynamic equilibrium. We are faced here with problems by far more complicated than in linear non-equilibrium thermodynamics, and at the same time this field of knowledge is of great interest due to the important applications in the field of hydrodynamics, chemical and especially biological phenomena. This is associated with the fact that any living organism is an example of an open thermodynamic system in an extremely non-equilibrium state—there exist at the boundary of a cell (not speaking of the living organism as a whole) large gradients of concentrations of chemical components, temperatures, pressures, fields, etc. In the last few years a considerable advance has been achieved in the elaboration of the thermodynamics of strongly non-equilibrium states, now representing a rapidly developing field of physics. Nevertheless, much is yet to be done in this direction before it will be possible to speak of a more or less orderly and complete section of thermodynamics.

The principal result obtained in studying the states far from equilibrium consists in the following. The total entropy production

$$P_S = \int \sigma_S \, d^3r = \int \sum_k Y^{(k)} X^{(k)} \, d^3r \qquad (101.1)$$

was seen above to be of minimum importance to actually realized steady-state processes with small deviations from equilibrium.

In proving this theorem, wide use was made of the linear relation between fluxes and forces and of Onsager's reciprocal relations. Both these concepts become invalid for the states far from equilibrium. and the theorem on the minimum of P_S in the stationary state in the general case becomes invalid.

If, however, we separate the rate of variation of entropy production into two terms,

$$\frac{\partial P_S}{\partial t} = \frac{\partial_X P_S}{\partial t} + \frac{\partial_Y P_S}{\partial t} = \int \sum_k Y^{(k)} \frac{\partial X^{(k)}}{\partial t} d^3r + \int \sum_k \frac{\partial Y^{(k)}}{\partial t} X^{(k)} d^3r, \tag{101.2}$$

the first of which represents the rate of variation of entropy production due to the change in the thermodynamic forces, and the second results from the change in the fluxes, then for systems in which convection is absent the first term can be shown to be non-positive:

$$\frac{\partial_X P_S}{\partial t} = \int \sum_k Y^{(k)} \frac{\partial X^{(k)}}{\partial t} d^3r \leqslant 0. \tag{101.3}$$

Due to the generality of the statement expressed by Eq. (101.3), the authors of the theorem (P. Glansdorff and I. Prigogine) called it the universal criterion of evolution.

The proof of this theorem [50] will not be given here, and we shall only illustrate it by considering the example of heat conduction in a solid with a constant volume and fixed boundary temperatures. Making use of the Gauss theorem, we have

$$\frac{\partial_X P_S}{\partial t} = \int \mathbf{L} \frac{\partial}{\partial t} [\nabla (T^{-1})] d^3r = \oiint \frac{\partial}{\partial t} (T^{-1}) \mathbf{L} d\sigma - \int \frac{\partial}{\partial t} (T^{-1}) \nabla \mathbf{L} d^3r.$$

The surface integral vanishes and $\nabla \mathbf{L} = -\rho c \partial T/\partial t$ suggests that the second term should be reduced to

$$\frac{\partial_X P_S}{\partial t} = -\int \rho c \frac{\left(\frac{\partial T}{\partial t}\right)^2}{T^2} d^3r \leqslant 0. \tag{101.4}$$

For the states close to equilibrium the criterion (101.3) will be shown to lead to the theorem on the minimum entropy production. Indeed, in the linear domain $Y^{(k)} = \sum_j L_{kj} X^{(j)}$ and

$$\sum_k Y^{(k)} \frac{\partial X^{(k)}}{\partial t} = \sum_{k,\, j} L_{kj} X^{(j)} \frac{\partial X^{(k)}}{\partial t} = \sum_{k,\, j} X^{(j)} \frac{\partial}{\partial t} (L_{kj} X^{(k)})$$

$$= \sum_j X^{(j)} \frac{\partial Y^{(j)}}{\partial t}.$$

(use was made of Onsager's reciprocal relations and the constancy of L_{kj}). Thus, both terms in Eq. (101.2) turn out to be equal, and Eq. (101.3) is equivalent to the inequality $\partial P_S/\partial t \leqslant 0$.

A number of authors, I. Prigogine and P. Glansdorffo in particular. have elaborated a detailed theory for phenomena in highly non-equilibrium systems. The component elements of this theory include Lyapunov's theory of stability and the generalized theory of fluctuations, in addition to classical balance equations and ordinary thermodynamic conditions for stability.

This theory cannot be treated here in great detail, and interested readers are referred to the very profound and interesting work by P. Glansdorff and I. Prigogine [50]. It is, however, of help to make a brief review of the ideas embodied in the results obtained in this work.

A serious disadvantage of criterion (101.3) consists in that it contains an inequality for the inexact differential $d_X P_S$, which makes impossible the introduction of such a chemical potential, the function of state, that would have an extremum in a stationary state as is the case with entropy S, free energy F, the Gibbs potential Φ at small deviations from equilibrium. It is possible, however, to introduce local potentials possessing extremum properties in some concrete problems in the highly non-equilibrium domain and reduce the problem of system's behaviour to a variational problem.

It should also be stressed that in a domain far from equilibrium the equations to which one succeeds to reduce the problem turn out to be nonlinear. In fact, a similar situation is often encountered when dealing with small deviations from equilibrium. An example from fluid dynamics are the Navier-Stokes nonlinear equations. Nonlinear situations are often observed in chemistry, where the kinetic equations relating the rates of reactions are usually nonlinear. For instance, even on the simplest assumption that dissociation and recombination are only due to collisions, for the reaction $A_2 \rightleftarrows 2A$ the kinetic equation for the number of molecules N_{A_2} has the following form:

$$\frac{dN_{A_2}}{dt} = -\alpha N_{A_2}^2 - \beta N_{A_2}(N_0 - 2N_{A_2}) + \gamma (N_0 - 2N_{A_2})^2,$$

$$N_0 = N_A + 2N_{A_2} = \text{const}.$$

The basic idea of the result obtained in the briefly outlined investigations is as follows. As a thermodynamic system goes away from equilibrium, it loses stability, and small fluctuations may lead to new spatial and time structures that are impossible near equilibrium. Simplest examples from fluid dynamics are the cellular structure of convective fluxes in a non-uniformly heated fluid, the appearance of turbulence, etc. In all these cases we observe

ordered motion of large groups of molecules, which had extremely low probability in the weakly non-equilibrium region and becomes the basic state in the region far from equilibrium.

The results obtained in investigating chemical reactions are of a still greater interest and of profound importance. A spontaneous origination of ordered structures with non-uniform, quasi-periodical spatial distribution of mixture components becomes possible in the region far from equilibrium. The time ordering of reactions in the case when periodical or quasi-periodical conditions appear is also possible. The two cases of ordering have been detected for various reactions and experiments.

The recognition of the possible origination of space- and time-ordered structures in regions far from thermodynamic equilibrium is of fundamental importance.

The two greatest theories developed in 19th century, that is the thermodynamics of equilibrium and weakly non-equilibrium systems and Darwin's theory of evolution, for a long time were assumed to be contradicting to one another. The second law of thermodynamics, stating that the entropy of an isolated (closed) system can only increase in the course of non-equilibrium processes or remain constant in equilibrium, corresponds to a tendency to randomization, which permits us to refer to equilibrium thermodynamics as to the theory of "structural breakdown". On the other hand, the theory of evolution states that "self-organization" of matter, the origination of more and more intricate self-reproducing structures takes place in nature. In this connection the speculative "theories" appeared, according to which the laws of thermodynamics and the second law, in particular, are not applicable to living matter. It is clear that the law of increase in entropy, pertaining to closed systems, is not applicable to living organisms that exchange energy and matter with the surrounding medium.

However, only in connection with the latest advances in non-equilibrium thermodynamics it has been shown that in open systems that are in states far from equilibrium self-organizing processes occur with the formation of time-recurring and spatially ordered structures. According to [51], the recording of information with the aid of some code may appear in some still more intricate systems, and later on this code controls the self-reproduction of these structures.

It is clear from the above that the development of non-equilibrium thermodynamics is of paramount importance for the solution of problems associated with the origin of life.

MATHEMATICAL APPENDIX

I. Jacobians (Functional Determinants)

Let us consider on a plane of variables (x, y) two families of curves: ξ-family ($\xi = \text{const}$) and η-family ($\eta = \text{const}$), where ξ and η are specified by the equations

$$\xi = \tilde{A}x + \tilde{B}y, \quad \eta = \tilde{C}x + \tilde{D}y \tag{I.1}$$

[Fig. 118 (*a*)]. On the plane of variables ξ, η, on the contrary, we have two families of curves: $x = \text{const}$ and $y = \text{const}$ [Fig. 118 (*b*)], where x and y are found from the equations

$$x = A\xi + B\eta, \quad y = C\xi + D\eta \tag{I.2}$$

and the matrix $\begin{vmatrix} A & B \\ C & D \end{vmatrix}$ is reciprocal to $\begin{vmatrix} \tilde{A} & \tilde{B} \\ \tilde{C} & \tilde{D} \end{vmatrix}$.

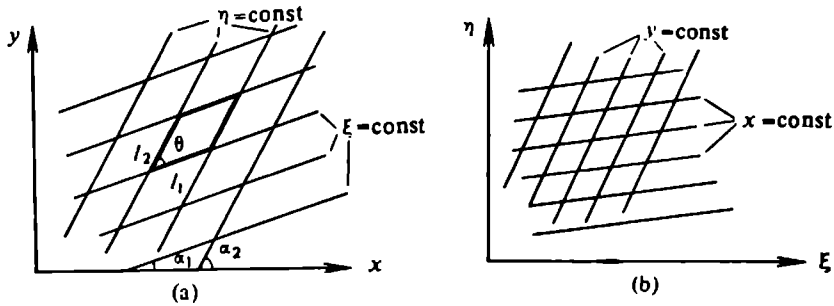

FIG. 118

Let us find the area of the parallelogram shown in Fig. 118 (*a*) by the solid line and formed by the intersection of two lines of the ξ-family,

$$\tilde{A}x + \tilde{B}y = \xi \text{ and } \tilde{A}x + \tilde{B}y = \xi + \Delta\xi$$

with the two lines of the η family,

$$\tilde{C}x + \tilde{D}y = \eta \text{ and } \tilde{C}x + \tilde{D}y = \eta + \Delta\eta.$$

We have

$$\Delta\sigma = l_1 l_2 |\sin\theta| = l_1 l_2 |\sin(\alpha_1 - \alpha_2)|$$
$$= l_1 l_2 |\sin\alpha_1 \cos\alpha_2 - \cos\alpha_1 \sin\alpha_2|. \tag{I.3}$$

Since

$$l_2 \sin\alpha_2 = \Delta y_\xi, \quad l_2 \cos\alpha_2 = \Delta x_\xi,$$
$$l_1 \sin\alpha_1 = \Delta y_\eta, \quad l_1 \cos\alpha_1 = \Delta x_\eta$$

(the indices ξ and η indicate, as usual, the constancy of ξ and η respectively), then Eq. (I.3) yields

$$\Delta\sigma = |\Delta x_\xi \Delta y_\eta - \Delta x_\eta \Delta y_\xi| = |AD - BC|\,\Delta\xi\,\Delta\eta = \left\|\begin{matrix} A & B \\ C & D \end{matrix}\right\| \Delta\xi\,\Delta\eta. \quad \text{(I.4)}$$

Let there be given now on the plane of variables x and y two sets of curves with the equations $\xi = \text{const}$, $\eta = \text{const}$ (Fig. 119), where

$$\xi = \xi(x, y), \quad \eta = \eta(x, y), \quad \text{(I.5)}$$

and, conversely, given on plane (ξ, η) are curves $x = \text{const}$, $y = \text{const}$, where $x(\xi, \eta)$, $y(\xi, \eta)$ are functions inverse to those expressed by formulae (I.5):

$$x = x(\xi, \eta), \quad y = y(\xi, \eta). \quad \text{(I.6)}$$

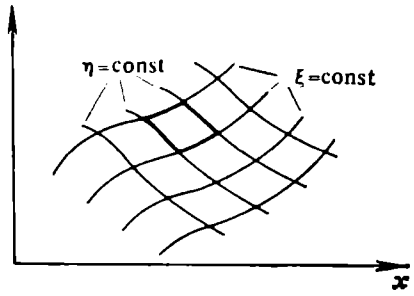

FIG. 119

The correspondence between the pairs (x, y) and (ξ, η) is assumed here to be one-to-one—for each point on the (x, y) plane there corresponds one and only one point on the (ξ, η) plane (this means that neither the curves $\xi = \text{const}$ nor the curves $\eta = \text{const}$ intersect each other, and each curve of the ξ-family intersects each curve of the η-family at one and only one point). Then, Eq. (I.6) is used to find, correct the first-order infinitesimals, the linear (local) relation between the differentials of the quantities x, y, ξ, η:

$$\begin{aligned} dx &= \frac{\partial x(\xi, \eta)}{\partial \xi}\, d\xi + \frac{\partial x(\xi, \eta)}{\partial \eta}\, d\eta, \\ dy &= \frac{\partial y(\xi, \eta)}{\partial \xi}\, d\xi + \frac{\partial y(\xi, \eta)}{\partial \eta}\, d\eta. \end{aligned} \quad \text{(I.7)}$$

It is seen that the area of the infinitely small parallelogram formed by the intersection of curves $\xi(x, y) = \xi$, $\xi(x, y) = \xi + d\xi$ with the curves $\eta(x, y) = \eta$, $\eta(x, y) = \eta + d\eta$ can be found by formula (I.4), if one replaces the coefficients A, B, C, D by $\partial x/\partial\xi$, $\partial x/\partial\eta$, $\partial y/\partial\xi$, $\partial y/\partial\eta$ respectively. We arrive then at the concept of the *functional determinant* (Jacobian) for two variables, which will be denoted by the letter D:

$$D = \frac{\partial(x, y)}{\partial(\xi, \eta)} = \left|\begin{matrix} \dfrac{\partial x}{\partial \xi} & \dfrac{\partial x}{\partial \eta} \\ \dfrac{\partial y}{\partial \xi} & \dfrac{\partial y}{\partial \eta} \end{matrix}\right| = \frac{\partial x}{\partial \xi}\frac{\partial y}{\partial \eta} - \frac{\partial x}{\partial \eta}\frac{\partial y}{\partial \xi}. \quad \text{(I.8)}$$

The geometrical meaning of the Jacobian is that the absolute value of D gives the coefficient of the change in the elementary area upon passing from the xy-plane to the $\xi\eta$-plane: the elementary area $dx\,dy$ passes into

$$d\sigma = |D|\,d\xi\,d\eta. \tag{I.9}$$

Let us point out some important properties of Jacobians.

1. $$\frac{\partial(x, y)}{\partial(\xi, \eta)} = -\frac{\partial(y, x)}{\partial(\xi, \eta)} = -\frac{\partial(x, y)}{\partial(\eta, \xi)}. \tag{I.10}$$

2. The Jacobian multiplication theorem:

$$\frac{\partial(x, y)}{\partial(u, v)} = \frac{\partial(x, y)}{\partial(\xi, \eta)}\,\frac{\partial(\xi, \eta)}{\partial(u, v)}. \tag{I.11}$$

The theorem stems from the known formulae of differential calculus,

$$\left(\frac{\partial x}{\partial u}\right)_v = \left(\frac{\partial x}{\partial \xi}\right)_\eta \left(\frac{\partial \xi}{\partial u}\right)_v + \left(\frac{\partial x}{\partial \eta}\right)_\xi \left(\frac{\partial \eta}{\partial u}\right)_v,$$

$$\left(\frac{\partial x}{\partial v}\right)_u = \left(\frac{\partial x}{\partial \xi}\right)_\eta \left(\frac{\partial \xi}{\partial v}\right)_u + \left(\frac{\partial x}{\partial \eta}\right)_\xi \left(\frac{\partial \eta}{\partial v}\right)_u$$

and, by analogy, for the derivatives $(\partial y/\partial u)_v$, $(\partial y/\partial v)_u$.

3. Substituting these expressions into the right-hand side of Eq. (I.11), we obtain an identity. The expression for a reciprocal Jacobian follows, in particular, from Eq. (I.11). Assuming $u = x$, $v = y$, we have

$$\frac{\partial(\xi, \eta)}{\partial(x, y)} = \frac{1}{\dfrac{\partial(x, y)}{\partial(\xi, \eta)}}. \tag{I.12}$$

4. We assume $y \equiv \eta$. Then $\left(\frac{\partial y}{\partial \xi}\right)_\eta = 0$, $\left(\frac{\partial y}{\partial \eta}\right)_\xi = 1$,

$$\frac{\partial(x, y)}{\partial(\xi, y)} = \begin{vmatrix} \left(\frac{\partial x}{\partial \xi}\right)_\eta & 0 \\ 0 & 1 \end{vmatrix} = \left(\frac{\partial x}{\partial \xi}\right)_y \tag{I.13}$$

and, by analogy,

$$\frac{\partial(x, y)}{\partial(x, \eta)} = \left(\frac{\partial y}{\partial \eta}\right)_x. \tag{I.14}$$

The behaviour of the Jacobian of transformation $(x, y) \to (\xi, \eta)$ on the xy- or $\xi\eta$-plane is directly associated with the question concerning the existence of one-to-one correspondence between points on the xy- and $\xi\eta$-planes. This problem is of paramount importance in thermodynamics due to the wide use of geometrical representations (points, lines, areas, etc.) on P-V, T-S, T-V, etc. planes.

There exists the following important theorem: if at point x_0y_0 on the xy-plane, corresponding to the point $\xi_0\eta_0$ on the $\xi\eta$-plane,

the Jacobians $\partial(\xi, \eta)/\partial(x, y)$ and $\partial(x, y)/\partial(\xi, \eta)$ differ from zero, there exists a one-to-one correspondence between points in the immediate neighbourhood of point x_0y_0 and points in the small neighbourhood of point $\xi_0\eta_0$. For each point of the first domain there exists one and only one point in the second domain, and vice versa.

This theorem is a direct corollary of the known Cramer's rule of the linear equation algebra. On condition that $\partial(x, y)/\partial(\xi, \eta) \neq 0$, the system of equations (I.7) has one definite solution with respect to the unknown $d\xi$, $d\eta$ at given dx, dy. This means that for a certain displacement on the xy-plane in the vicinity of point x_0y_0 there corresponds one definite displacement on the $\xi\eta$-plane in the vicinity of point $\xi_0\eta_0$. In particular, at $dx = 0$, $dy = 0$ the system (I.7) has only one solution $d\xi = 0$, $d\eta = 0$.

The same can be said about a system inverse to the system of equations (I.7), if the Jacobian $\partial(\xi, \eta)/\partial(x, y)$ differs from zero at point x_0y_0.

The above theorem is of a local nature, but if the Jacobians $\partial(x, y)/\partial(\xi, \eta)$ and $\partial(\xi, \eta)/\partial(x, y)$ differ from zero over the entire xy- and $\xi\eta$-planes, then there exists a one-to-one correspondence between points in the small neighbourhood of any points on these planes. In order to draw the conclusion that there exists a one-to-one correspondence between finite (not infinitely small) domains on the xy- and $\xi\eta$-planes, some supplementary conditions are required that are not discussed here, but assumed to be usually satisfied in thermodynamics.

II. Stirling's Formula

Stirling's formula gives an approximate value for $N!$ at large N. Let us proceed from the formula

$$N! = \Gamma(N + 1) = \int_0^\infty e^{-t} t^N \, dt. \tag{II.1}$$

We replace the variables, $t = N(1 + z)$:

$$N! = N^{N+1} e^{-N} \int_{-1}^{\infty} e^{-zN} (1 + z)^N \, dz,$$

and make a new replacement

$$(1 + z) e^{-z} = e^{-u^2/2}. \tag{II.2}$$

We obtain

$$N! = N^{N+1} e^{-N} \int_{-\infty}^{\infty} e^{-Nu^2/2} \frac{dz}{du} \, du.$$

At large values of N the slowly varying factor dz/du can be replaced by its value at $u = 0$ ($z = 0$) equal to unity. Expanding e^{-z} and $e^{-u^2/2}$ in Eq. (II.2), we see that $u \approx z$ at small u and z. As a result, we find

$$N! = N^{N+1}e^{-N} \int_{-\infty}^{\infty} e^{-Nu^2/2}\, du$$

and, using formula (IV.3), we obtain

$$N! = (2\pi N)^{1/2}\left(\frac{N}{e}\right)^N, \tag{II.3}$$

$$\ln N! = N \ln N - N + 1/2 \ln (2\pi N). \tag{II.4}$$

At large values of N the last term in Eq. (II.4) is small compared with each of the first two (for $N = 10^3$ it already amounts to about 0.4%). For this reason in statistical physics formulae (II.3) and (II.4) are used in a simplified form:

$$N! = \left(\frac{N}{e}\right)^N, \tag{II.5}$$

$$\ln N! = N \ln N - N. \tag{II.6}$$

III. Lagrange's Method of Finding the Conditional Extremum

Let us consider the problem of finding the extremum of the function $f(N_1, N_2, \ldots, N_m)$ at some supplementary conditions imposed on the variables $N_1, N_2, \ldots, N_m$, i.e. the problem on the *conditional extremum*. It should be recalled that under some conditions

$$\varphi_i (N_1, \ldots, N_m) = 0, \quad i = 1, 2, \ldots, n \quad (n < m) \tag{III.1}$$

the extremum of the function $f(N_1, \ldots, N_m)$ can be found with the aid of the *Lagrange method of multipliers*, the essence of which is as follows.

In the presence of n conditions (III.1) only $m - n$ quantities N_i are independent, and the remaining n can be found from conditions (III.1). We can assume without loss of generality the quantities $N_1, \ldots, N_n$ to be interdependent. Let us write the first differentials of the functions $f(N_1, \ldots, N_m)$ and $\varphi_i (N_1, \ldots, N_m)$. At the extreme point we have

$$df = \sum_{k=1}^{m} \frac{\partial f}{\partial N_k}\, dN_k = 0 \tag{III.2}$$

and by virtue of conditions (III.1),

$$d\varphi_l = \sum_{k=1}^{m} \frac{\partial \varphi_l}{\partial N_k} dN_k = 0. \tag{III.3}$$

Let us multiply each of the relationships (III.3) by the so far arbitrary factors λ_k and subtract the result from Eq. (III.2), obtaining

$$d\left(f - \sum_i \lambda_l \varphi_l\right) = \sum_{k=1}^{m} \left[\frac{\partial f}{\partial N_k} - \sum_{i=1}^{n} \lambda_l \frac{\partial \varphi_l}{\partial N_k}\right] dN_k = 0. \tag{III.4}$$

Let us now choose the numbers λ_i so that the coefficients at n interdependent differentials vanish, i.e. from the conditions

$$\frac{\partial f}{\partial N_k} - \sum_{i=1}^{n} \lambda_l \frac{\partial \varphi_l}{\partial N_k} = 0 \quad (k = 1, 2, \ldots, n).$$

Since the remaining N_k ($k = n + 1, n + 2, \ldots, m$) are independent, their coefficients in expression (III.4) must also vanish, and we have

$$\frac{\partial f}{\partial N_k} - \sum_{i=1}^{n} \lambda_l \frac{\partial \varphi_l}{\partial N_k} = 0 \tag{III.5}$$

at any k from unity to m.

Thus, finding the conditional extremum of $f(N_l)$ under conditions expressed by formula (III.1) reduces to finding the absolute extremum of the function $f - \sum_{i=1}^{n} \lambda_i \varphi_l$. To find $n + m$ unknowns (m coordinates of the extreme point $N_1^{(0)}, N_2^{(0)}, \ldots, N_m^{(0)}$ and n Lagrangian multipliers $\lambda_1, \ldots, \lambda_n$) we have the same number of equations: m equations (III.3) and n conditions (III.1).

IV. Integrals J_n

Let us consider an integral of the kind

$$J_n = \int_0^{\infty} x^n e^{-\alpha x^2} dx, \tag{IV.1}$$

where n is a non-negative integer. The substitution $y = \alpha x^2$ is used to reduce integral (IV.1) to

$$J_n = \frac{1}{2} \alpha^{-(n+1)/2} \int_0^{\infty} e^{-y} y^{(n-1)/2} dy = \frac{1}{2} \alpha^{-(n+1)/2} \Gamma\left(\frac{n+1}{2}\right). \tag{IV.2}$$

With even $n = 2m$ we have

$$J_{2m} = \frac{(2m-1)!!}{2^{m+1}} \sqrt{\frac{\pi}{\alpha^{2m+1}}}, \tag{IV.3}$$

and with odd $n = 2m + 1$,

$$J_{2m+1} = \frac{m!}{2\alpha^{m+1}}.$$

The integral $J'_n = \int_{-\infty}^{\infty} x^n e^{-\alpha x^2}\, dx$ equals zero when n is odd and equals $2J_n$ when n is even.

V. Probability Function erf (x)

The probability (error) integral, or the Gauss error function erf (x), is determined by the formula

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \tag{V.1}$$

and possesses the obvious properties

$$\operatorname{erf}(0) = 0, \quad \operatorname{erf}(\infty) = 1, \tag{V.2}$$

$$\operatorname{erf}(-x) = -\operatorname{erf}(x). \tag{V.3}$$

The asymptotic expansion of erf (x) at $x \ll 1$, outlined in Sec. 41, has the following form:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} x \left(1 - \frac{x^2}{2} + \frac{x^4}{10} - \cdots\right). \tag{V.4}$$

At $x \gg 1$ the following asymptotic representation of erf (x) is valid:

$$\operatorname{erf}(x) \approx 1 - \frac{e^{-x^2}}{\sqrt{\pi} x}. \tag{V.5}$$

Tables of the probability functions can be found, for instance, in [5].

VI. Properties of Function $\theta(x) = \sum_{n=-\infty}^{\infty}{}' e^{-\pi n^2 x}$

Let us prove the validity of the functional equation from Sec. 45 for the function $\theta(x)$. We introduce the function

$$S(y, x) = \sum_{n=-\infty}^{\infty}{}' e^{-\pi (n+y)^2 x}. \tag{VI.1}$$

Being a function of y, it is periodic with a period equal to unity and can be expanded into a Fourier series:

$$S(y, x) = \sum_{m=-\infty}^{\infty} a_m(x)\, e^{-2\pi i m y}, \tag{VI.2}$$

where

$$a_m(x) = \int_0^1 S(t, x)\, e^{-2\pi i m t}\, dt = \int_0^1 \sum_{n=-\infty}^{\infty} e^{-\pi (n+t)^2 x - 2\pi i m t}\, dt.$$

Changing the sequence of summation and integration and multiplying the integrand by $e^{-2\pi i n m} = 1$, we obtain

$$\begin{aligned} a_m(x) &= \sum_{n=-\infty}^{\infty} \int_0^1 e^{-\pi (n+t)^2 x - 2\pi i m (n+t)}\, dt \\ &= \sum_{n=-\infty}^{\infty} \int_n^{n+1} e^{-\pi z^2 x - 2\pi i m z}\, dz = \int_{-\infty}^{\infty} e^{-\pi z^2 x - 2\pi i m z}\, dz \\ &= e^{-\pi m^2/x} \int_{-\infty}^{\infty} e^{-\pi x \left(z + \frac{im}{x}\right)^2} dz = \frac{e^{-\frac{\pi m^2}{x}}}{\sqrt{x}} \end{aligned} \tag{VI.3}$$

[since $\int_{-\infty+i\sigma}^{\infty+i\sigma} e^{-\alpha z^2}\, dz$, taken along a straight line parallel to the real axis, is equal to $\sqrt{\frac{\pi}{\alpha}}$ according to formula (IV.3)]. Substituting (VI.3) into (VI.2), we have

$$S(y, x) = \frac{1}{\sqrt{x}} \sum_{m=-\infty}^{\infty} e^{-\frac{\pi m^2}{x} + 2\pi i m y}, \tag{VI.4}$$

whence at $y = 0$ we obtain the equation (see Sec. 45)

$$\theta(x) = \frac{1}{\sqrt{x}} \sum_{m=-\infty}^{\infty} e^{-\frac{\pi m^2}{x}} = \frac{1}{\sqrt{x}}\, \theta\left(\frac{1}{x}\right). \tag{VI.5}$$

VII. Integrals K_n and K'_n

Let us evaluate an integral of the kind

$$K_n = \int_0^{\infty} \frac{x^n\, dx}{e^x - 1},$$

where n is an integer or half-integer. We have

$$(e^x-1)^{-1}=e^{-x}(1-e^{-x})^{-1}=\sum_{k=0}^{\infty}e^{-(k+1)x},$$

whence

$$K_n=\int_0^{\infty}\sum_{l=0}^{\infty}x^n e^{-(l+1)x}\,dx=\sum_{l=0}^{\infty}\int_0^{\infty}x^n e^{-(l+1)x}\,dx=\sum_{l=0}^{\infty}(l+1)^{-n-1}\int_0^{\infty}e^{-t}t^n\,dt$$

$$=\Gamma(n+1)\sum_{l=0}^{\infty}(l+1)^{-n-1}=\Gamma(n+1)\,\zeta(n+1), \quad \text{(VII.1)}$$

where $\zeta(r)=\sum_{k=1}^{\infty}k^{-r}$ and ζ is Riemann's function.

In particular, we have

1. $n=1$, $K_1=\int_0^{\infty}\frac{x\,dx}{e^x-1}=\Gamma(2)\,\zeta(2)$, since $\Gamma(2)=1$, $\zeta(2)=\frac{\pi^2}{6}$ (see, for instance [5]), then

$$K_1=\pi^2/6. \quad \text{(VII.2)}$$

2. $n=3$, $K_3=\int_0^{\infty}\frac{x^3\,dx}{e^x-1}=\Gamma(4)\,\zeta(4)$. (VII.3)

Since $\Gamma(4)=3!$ and $\zeta(4)=\pi^4/90$, then

$$K_3=\pi^4/15. \quad \text{(VII.4)}$$

3. $n=\frac{1}{2}$, $K_{1/2}=\int_0^{\infty}\frac{x^{1/2}\,dx}{e^x-1}=\Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right)$.

Since $\Gamma\left(\frac{3}{2}\right)=\frac{1}{2}\Gamma\left(\frac{1}{2}\right)=\frac{\sqrt{\pi}}{2}$ and $\zeta\left(\frac{3}{2}\right)=2.612$, then $K_{1/2}=2.33$.

4. $n=\frac{3}{2}$, $K_{3/2}=\int_0^{\infty}\frac{x^{3/2}\,dx}{e^x-1}=\Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right)$. (VII.5)

Since $\Gamma\left(\frac{5}{2}\right)=\frac{3}{2}\Gamma\left(\frac{3}{2}\right)=\frac{3\sqrt{\pi}}{4}$ and $\zeta\left(\frac{5}{2}\right)=1.341$, then

$$K_{3/2}=1.78. \quad \text{(VII.6)}$$

Let us also find integrals of the kind

$$K_n'=\int_0^{\infty}\frac{x^n e^x\,dx}{(e^x-1)^2} \quad (n>1).$$

We have

$$K'_n = \sum_{l=0}^{\infty} (l+1) \int_0^{\infty} x^n e^{-(l+1)x}\, dx$$

$$= \sum_{l=0}^{\infty} (l+1)^{-n} \int_0^{\infty} e^{-t} t^n\, dt = \Gamma(n+1)\, \zeta(n). \quad \text{(VII.7)}$$

In particular,

$$K'_{3/2} = \Gamma\left(\frac{5}{2}\right) \xi\left(\frac{3}{2}\right) = 3.48, \quad K'_{5/2} = \Gamma\left(\frac{7}{2}\right) \xi\left(\frac{5}{2}\right) = 4.45. \quad \text{(VII.8)}$$

VIII. Dirac's Delta-Function $\delta(x)$ and Step Function $\sigma(x)$

Let us introduce the improper or generalized function $\delta(x)$ specified by the conditions

$$\delta(x) = \begin{cases} 0 & \text{for } x \neq 0, \\ \infty & \text{for } x = 0, \end{cases} \quad \text{(VIII.1)}$$

$$\int_a^b \delta(x)\, dx = \begin{cases} 1 & \text{for } x = 0 \in (a, b), \\ 0 & \text{for } x = 0 \notin (a, b). \end{cases} \quad \text{(VIII.2)}$$

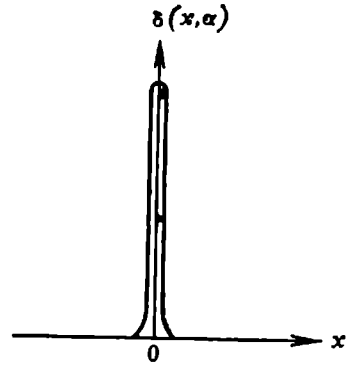

FIG. 120

More exactly, the function $\delta(x)$ must be defined as the limit of some continuous function $\delta(x, \alpha)$ having a sharp maximum at $x=0$, with an area equal to unity (Fig. 120), when the parameter α tends to zero (with the height of the peak infinitely increasing and its width infinitely decreasing. Therefore, strictly speaking, the δ-function has a meaning only as an integrand, and the limit transition $\alpha \to 0$ must be made after evaluation of the integral. Usually, no errors appear when the δ-function is treated as a common classical-analysis function.

Let us examine several examples of continuous functions $\delta(x, \alpha)$ that pass in the limit $\alpha \to 0$ into the δ-function:

$$\delta(x, \alpha) = \frac{\alpha}{\pi (x^2 + \alpha^2)} = \frac{d}{dx}\left(\frac{1}{\pi} \arctan \frac{x}{\alpha}\right), \quad \text{(VIII.3)}$$

$$\delta(x, \alpha) = \frac{e^{x/\alpha}}{\alpha (e^{x/\alpha} + 1)^2} = \frac{d}{dx}\left(\frac{1}{e^{-x/\alpha} + 1}\right). \quad \text{(VIII.4)}$$

The delta-function can be considered as the derivative of the discontinuous step function σ specified by the equation

$$\sigma(x) = \begin{cases} 1 & \text{for } x > 0, \\ 0 & \text{for } x < 0. \end{cases} \tag{VIII.5}$$

Some properties of δ-functions are given below without proof.

1. $$\delta(-x) = \delta(x). \tag{VIII.6}$$

2. $$\int_a^b \delta(x-x')\, f(x)\, dx = \int_a^b \delta(x-x')\, f(x')\, dx = \begin{cases} f(x) & \text{for } x = x' \in (a, b), \\ 0 & \text{for } x = x' \notin (a, b). \end{cases} \tag{VIII.7}$$

3. $$\delta[\varphi(x)] = \sum_r \frac{\delta(x-x_r)}{|\varphi'(x_r)|}, \tag{VIII.8}$$

where x_r are simple roots of equation $\varphi(x) = 0$ within the integration domain. Therefore, we have

4. $$\int_a^b f(x)\, \delta[\varphi(x)]\, dx = \sum_r \frac{f(x_r)}{|\varphi'(x_r)|}. \tag{VIII.9}$$

In particular,

5. $$\delta(ax) = \frac{1}{a}\, \delta(x), \tag{VIII.10}$$

6. $$\delta(x^2 - a^2) = \frac{\delta(x-a) + \delta(x+a)}{2|a|}. \tag{VIII.11}$$

Similarly, the derivative $\delta'(x)$ can be defined as the limit of a certain continuous function, and for this derivative the following formulae are valid:

7. $$\delta'(-x) = -\delta'(x), \tag{VIII.12}$$

8. $$\int_a^b f(x)\, \delta'(x-x')\, dx = \begin{cases} -\left(\frac{\partial f}{\partial x}\right)_{x=x'} & \text{for } x' \in (a, b), \\ 0 & \text{for } x' \notin (a, b). \end{cases} \tag{VIII.13}$$

The concept of the δ-function can be extended to an n-dimensional space with the aid of the formula

$$\delta(x_1, x_2, \ldots, x_n) = \delta(x_1)\, \delta(x_2) \ldots \delta(x_n), \tag{VIII.14}$$

then the practical realizations of the δ-function and its properties can readily be applied to n-dimensional spaces.

IX. Integrals L_n

Let us calculate the integral

$$L_n = \int_0^\infty \frac{x^n\,dx}{e^x+1}.$$

Expanding $(e^x + 1)^{-1}$ into a series in e^{-x}, we find

$$L_n = \sum_{l=0}^{\infty}(-1)^l \int_0^\infty x^n e^{-(l+1)x}\,dx = \sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)^{n+1}}\int_0^\infty e^{-t}t^n\,dt$$

$$= \Gamma(n+1)\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)^{n+1}}. \quad \text{(IX.1)}$$

The sum of the series in formula (IX.1) can be expressed in terms of the Riemann ζ-function. For this purpose let us add to the unknown sum and subtract from it the same sum over odd values of l. We obtain

$$\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)^{n+1}} = \sum_{l=0}^{\infty}\frac{1}{(l+1)^{n+1}} - 2\sum_{m=0}^{\infty}\frac{1}{(2m+2)^{n+1}} = \zeta(n+1)(1-2^{-n})$$

and, substituting this into formula (IX.1), we find

$$L_n = (1-2^{-n})\,\Gamma(n+1)\,\zeta(n+1). \quad \text{(IX.2)}$$

Expression (IX.2) becomes indeterminate at $n = 0$, since $\zeta(1) = \infty$; at $n = 0$, however, we have

$$L_0 = \int_0^\infty \frac{dx}{e^x+1} = \int_1^\infty \frac{dy}{y(y+1)} = \ln 2.$$

At $n = 1/2$, 1 and 3 we find

$$L^{1/2} = (1-2^{-1/2})\,\Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right) = 0.673,$$

$$L_1 = \frac{1}{2}\,\Gamma(2)\,\zeta(2) = \frac{\pi^2}{12}, \quad \text{(IX.3)}$$

$$L_3 = \frac{7}{8}\,\Gamma(4)\,\zeta(4) = \frac{7\pi^4}{120}.$$

X. Integral M

Let us calculate the integral

$$M = \int_0^\infty \varphi(\varepsilon)\,f(\varepsilon)\,d\varepsilon, \quad \text{(X.1)}$$

where $f(\varepsilon)$ is the Fermi distribution function, equal to $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/T}+1}$, in the assumption that $T/\mu \ll 1$. Integrating by parts, we obtain

$$M = F(\infty) f(\infty) - F(0) f(0) - \int_0^\infty F(\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon, \tag{X.2}$$

where

$$F(\varepsilon) = \int_0^\varepsilon \varphi(\varepsilon) d\varepsilon. \tag{X.3}$$

In all the cases of practical interest the term outside the integral in Eq. (X.2) is equal to zero, since $f(\infty) = 0$ and $F(0) = 0$; to be more exact, the validity of this assertion requires that as $\varepsilon \to \infty$ function $\varphi(\varepsilon)$ should not increase at a rate greater than $e^{\varepsilon/T}$, and as $\varepsilon \to 0$ it should not increase at a rate greater than ε^{-1}. Assuming these conditions to be satisfied, we have

$$M = \int_0^\infty \varphi(\varepsilon) f(\varepsilon) d\varepsilon = -\int_0^\infty F(\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon. \tag{X.4}$$

Let us turn to the integration variable $x = (\varepsilon - \mu)/T$:

$$M = -\int_{-\mu/T}^\infty F(\mu + Tx) \frac{\partial f}{\partial x} dx. \tag{X.5}$$

Let us examine the properties of the function $\frac{\partial f}{\partial x} = -\frac{e^x}{(e^x+1)^2}$. It can be readily seen that, first, it is an even function, $e^{-x}/(e^{-x}+1)^2 = e^x/(e^x+1)^2$, second, that the function rapidly, as $e^{-|x|}$, decreases with increasing absolute value of x, so that it noticeably differs from zero only in the vicinity of point $x = 0$ ($\varepsilon = \mu$). In consequence only small $|x|$ contribute appreciably to integral (X.5), and we can expand $F(\mu + Tx)$ into a series in x, limiting ourselves to the first terms of the expansion. By virtue of the inequality $\mu/T \gg 1$ we can replace the lower integration limit by $-\infty$ without any significant error. Then, we obtain

$$M = -\int_{-\infty}^\infty \left[F(\mu) + TF'(\mu) x + \frac{1}{2} T^2 F''(\mu) x^2 + \ldots\right] \frac{\partial f}{\partial x} dx$$

$$= F(\mu)\,[f(-\infty) - f(\infty)] - TF'(\mu) \int_{-\infty}^\infty x \frac{\partial f}{\partial x} dx$$

$$- \frac{1}{2} T^2 F''(\mu) \int_{-\infty}^\infty x^2 \frac{\partial f}{\partial x} dx \ldots.$$

We have $f(\infty) = 0$, $f(-\infty) = 1$; further $\int\limits_{-\infty}^{\infty} x \frac{\partial f}{\partial x}\, dx = 0$ (by virtue of the fact that the integrand is an odd function), and integrating by parts, we find

$$\int\limits_{-\infty}^{\infty} x^2 \frac{\partial f}{\partial x}\, dx = 2\int\limits_{0}^{\infty} x^2 \frac{\partial f}{\partial x}\, dx = -4\int\limits_{0}^{\infty} \frac{x\, dx}{e^x+1} = -4L_1 = -\frac{\pi^2}{3}.$$

Substituting $F(\varepsilon)$ from Eq. (X.3), we obtain a final result, presented below in two forms:

$$M = \int\limits_{0}^{\infty} \varphi(\varepsilon) f(\varepsilon)\, d\varepsilon = \int\limits_{0}^{\mu} \varphi(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6} T^2 \left(\frac{\partial \varphi}{\partial \varepsilon}\right)_{\varepsilon=\mu} + \ldots, \quad \text{(X.6)}$$

$$M = -\int\limits_{0}^{\infty} F(\varepsilon) \frac{\partial f}{\partial \varepsilon}\, d\varepsilon = F(\mu) + \frac{\pi^2}{6} T^2 \left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_{\varepsilon=\mu} + \ldots. \quad \text{(X.7)}$$

If $\varphi(\varepsilon)$ is a power function, $\varphi(\varepsilon) = \varepsilon^n$, then formula (X.6) acquires the following form:

$$M_n = \int\limits_{0}^{\infty} \varepsilon^n f(\varepsilon)\, d\varepsilon = \frac{\mu^{n+1}}{n+1}\left[1 + \frac{n(n+1)\,\pi^2}{6}\left(\frac{T}{\mu}\right)^2\right]. \quad \text{(X.8)}$$

XI. The Laplace Transform

Let there be given on a real axis the function $Z(\lambda)$, continuous and differentiable everywhere (except at some points where $Z(\lambda)$ and $Z'(\lambda)$ can have finite discontinuity jumps). Let $Z(\lambda)$ increase as $\lambda \to +\infty$ at a rate not higher than $e^{\alpha\lambda}$, and as $\lambda \to -\infty$, at a rate not higher than $e^{\beta\lambda}$, so that

$$\int\limits_{-\infty}^{\infty} e^{-\sigma\lambda} Z(\lambda)\, d\lambda$$

absolutely converges for $\beta > \sigma > \alpha$.

Let us consider under these conditions the function of complex variable E, specified by the equation

$$\rho(E) = \int\limits_{-\infty}^{\infty} e^{-\lambda E} Z(\lambda)\, d\lambda \qquad (\beta > \lambda > \alpha) \qquad \text{(XI.1)}$$

and try to find the inversion of this formula, i.e. to express $Z(\lambda)$ in terms of $\rho(E)$. Let us proceed from Fourier's transform

$$f(\lambda) = \int_{-\infty}^{\infty} \varphi(\mu)\, e^{-i\mu\lambda}\, d\mu, \tag{XI.2}$$

$$\varphi(\mu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\lambda)\, e^{i\mu\lambda}\, d\lambda, \tag{XI.3}$$

from which follows the Fourier integral formula

$$f(\lambda) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{-i\mu\lambda} \int_{-\infty}^{\infty} f(\nu)\, e^{i\nu\mu}\, d\nu. \tag{XI.4}$$

Substituting $f(\lambda) = e^{-\sigma\lambda} Z(\lambda)$ into formula (XI.4), we find

$$e^{-\sigma\lambda} Z(\lambda) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{-i\mu\lambda} \int_{-\infty}^{\infty} Z(\nu)\, e^{-\nu(\sigma - i\mu)}\, d\nu$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{-i\mu\lambda} \rho(\sigma - i\mu).$$

Introducing the integration variable $E = \sigma - i\mu$, we obtain

$$Z(\lambda) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} \rho(E)\, e^{\lambda E}\, dE \quad (\beta > \sigma > \alpha), \tag{XI.5}$$

i.e. the required inversion of formula (XI.1). Formulae (XI.1) and (XI.5) are referred to as the *Laplace bilateral transform*.

If $Z(\lambda) \equiv 0$ at $\lambda < 0$, we obtain from Eqs. (XI.1) and (XI.5) the formulae

$$\rho(E) = \int_{0}^{\infty} e^{-\lambda E} Z(\lambda)\, d\lambda \quad (\lambda > \alpha), \tag{XI.6}$$

$$Z(\lambda) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} e^{\lambda E} \rho(E)\, dE, \tag{XI.7}$$

that are referred to as the *Laplace unilateral transforms*.

XII. Integrals for Section 59

Let us consider the integral ($0 < \operatorname{Re} \lambda < 1$) and integrate it by parts

$$\int_{-\infty}^{\infty} \ln(1+e^{\zeta})\, e^{-\lambda\zeta}\, d\zeta = \frac{1}{\lambda} \int_{-\infty}^{\infty} \frac{e^{-\lambda\zeta}\, d\zeta}{e^{\zeta}+1}, \qquad \text{(XII.1)}$$

Upon substitution $e^{-\zeta} = x/(1-x)$, $d\zeta = -dx/x(1-x)$ the integral is reduced to

$$\frac{1}{\lambda} \int_0^1 x^{\lambda-1} (1-x)^{-\lambda}\, dx.$$

Comparing this with the formula for Euler's integral of the first kind,

$$B(p, q) = \int_0^1 x^{p-1} (1-x)^{q-1}\, dx = \frac{\Gamma(p)\,\Gamma(q)}{\Gamma(p+q)}$$

(see, for instance, [8]), we have

$$\int_{-\infty}^{\infty} \ln(1+e^{\zeta})\, e^{-\lambda\zeta}\, d\zeta = \frac{1}{\lambda} B(\lambda, 1-\lambda) = \frac{\Gamma(\lambda)\,\Gamma(1-\lambda)}{\lambda}.$$

Making use of the property of the Γ-function, $\Gamma(\lambda)\,\Gamma(1-\lambda) = \pi/\sin \pi\lambda$, we obtain

$$\int_{-\infty}^{\infty} \ln(1+e^{\zeta})\, e^{-\lambda\zeta}\, d\zeta = \frac{\pi}{\lambda \sin \pi\lambda}. \qquad \text{(XII.2)}$$

Applying to this integral the Laplace transform (XI.5), we find

$$\ln(1+e^{\zeta}) = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{\pi\lambda}{\sin \pi\lambda} \frac{e^{\lambda\zeta}}{\lambda^2}\, d\lambda. \qquad \text{(XII.3)}$$

(see Sec. 59). Now let us consider the integral

$$\int_{-\infty}^{\infty} \frac{e^{\zeta\lambda}\, d\zeta}{4\cosh^2 \frac{\zeta}{2}} = \int_{-\infty}^{\infty} \frac{e^{\zeta\lambda}\, d\zeta}{(e^{\zeta/2}+e^{-\zeta/2})^2} = \int_{-\infty}^{\infty} \frac{e^{\zeta\lambda}\, d\zeta}{e^{\zeta}+e^{-\zeta}+2}$$

and make the substitution $e^{\zeta} = x/(1-x)$, $d\zeta = dx/x(1-x)$, then

$$\int_{-\infty}^{\infty} \frac{e^{\zeta\lambda}\, d\zeta}{4\cosh^2 \frac{\zeta}{2}} = \int_0^1 x^{\lambda} (1-x)^{-\lambda}\, dx = B(1+\lambda,\ 1-\lambda)$$

$$= \frac{\Gamma(1+\lambda)\,\Gamma(1-\lambda)}{\Gamma(2)} = \lambda\Gamma(\lambda)\,\Gamma_1(1-\lambda) = \frac{\pi\lambda}{\sin \pi\lambda}. \qquad \text{(XII.4)}$$

We obtained formula (59.10) from Sec. 59. We have the obvious relation

$$\frac{1}{\lambda^2} = \int_0^\infty \zeta e^{-\lambda\zeta}\, d\zeta = \int_{-\infty}^{\infty} \zeta\sigma(\zeta)\, e^{-\lambda\zeta}\, \partial\zeta.$$

Using the inversion formula for the Laplace transform (XI.5), we obtain relation (59.9) from Sec. 59:

$$\frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{e^{\lambda\zeta}}{\lambda^2}\, d\lambda = \zeta\sigma(\zeta). \qquad \text{(XII.5)}$$

XIII. n-Dimensional Sphere

Let us calculate the volume and surface area of a sphere, and also the total solid angle in the n-dimensional space (Cartesian coordinates $x_1, x_2, \ldots, x_n$).

From dimensionality considerations it is clear that the volume of an n-dimensional sphere, i.e. the volume of the domain $x_1^2 + x_2^2 + \ldots + x_n^2 \leqslant R^2$, is equal to

$$V_n = C_n R^n, \qquad \text{(XIII.1)}$$

where C_n is a dimensionless constant to be determined. The simplest way of finding C_n consists in the following. Evaluate the integral

$$\int_0^\infty e^{-r^2}\, dV_n(r) = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\ldots+x_n^2)}\, dx_1\, dx_2 \ldots dx_n \qquad \text{(XIII.2)}$$

following the two methods: in spherical coordinates [the left-hand side of Eq. (XIII.2)] and in rectangular Cartesian coordinates [the right-hand side of Eq. (XIII.2)]. The right-hand side of the equation is expressed by the n-fold multiple Poisson integral

$$\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\ldots+x_n^2)}\, dx_1\, dx_2 \ldots dx_n$$

$$= \left(\int_{-\infty}^{\infty} e^{-x^2}\, dx \right)^n = \pi^{n/2}. \qquad \text{(XIII.3)}$$

Substituting for the left-hand side of Eq. (XIII.2) the expression following from Eq. (XIII.1), $dV_n(r) = nC_n r^{n-1}\, dr$, we obtain

$$nC_n \int_0^\infty e^{-r^2} r^{n-1}\, dr = \frac{nC_n}{2} \int_0^\infty e^{-y} y^{n/2-1}\, dy = \frac{1}{2}\, nC_n \Gamma\left(\frac{n}{2}\right). \qquad \text{(XIII.4)}$$

Equating expressions (XIII.3) and (XIII.4), we get

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)} \tag{XIII.5}$$

and

$$V_n = \frac{2\pi^{n/2}R^n}{n\Gamma(n/2)}. \tag{XIII.6}$$

At $n = 1, 2, 3$ we obtain the elementary formulae $V_1 = 2R$, $V_2 = \pi R^2$, $V_3 = \frac{4}{3}\pi R^3$.

The surface area of an n-dimensional sphere is found from the relationship $dV_n(R) = S_n(R)\,dR$,

$$S_n = \frac{2\pi^{n/2}R^{n-1}}{\Gamma(n/2)}. \tag{XIII.7}$$

At $n = 1, 2, 3$ we have $S_1 = 2$, $S_2 = 2\pi R$, $S_3 = 4\pi R^2$.

The total solid angle is obtained, assuming in formula (XIII.7) $R = 1$:

$$\Omega_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}. \tag{XIII.8}$$

In statistical physics one has to deal with the case when $n \gg 1$. Using Stirling's formula

$$\Gamma\left(\frac{n}{2}\right) \cong (2\pi)^{1/2}\,(n/2)^{(n-1)/2}e^{-n/2}, \tag{XIII.9}$$

with a logarithmic accuracy we find from Eqs. (XIII.6)-(XIII.8)

$$C_n = \left(\frac{2\pi e}{n}\right)^{n/2} \tag{XIII.10}$$

$$V_n(R) = \left(\frac{2\pi e}{n}\right)^{n/2} R^n, \tag{XIII.11}$$

$$S_n(R) = \left(\frac{2\pi e}{n}\right)^{n/2} R^{n-1}, \tag{XIII.12}$$

$$\Omega_n = \left(\frac{2\pi e}{n}\right)^{n/2}. \tag{XIII.13}$$

XIV. The Gauss Distribution for One and Two Variables

Let the probability distribution for the quantity x obey the law of normal (Gaussian) distribution,

$$dW(x) = Ae^{-\alpha x^2}dx \quad (-\infty < x < \infty). \tag{XIV.1}$$

The normalization condition $\int dW(x) = 1$ yields

$$A = \sqrt{\frac{\alpha}{\pi}}. \tag{XIV.2}$$

The mean value of the quantity x equals zero due to the symmetry of the Gaussian distribution,

$$\overline{x} = 0. \tag{XIV.3}$$

Let us find $\overline{x^2} = (Dx)^2$,

$$\overline{x^2} = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}\, dx = \frac{1}{2\alpha}. \tag{XIV.4}$$

Expressing α in terms of $\overline{x^2}$, we can present the Gaussian distribution in the form

$$dW(x) = \frac{1}{\sqrt{2\pi\overline{x^2}}}\, e^{-x^2/2\overline{x^2}}\, dx. \tag{XIV.5}$$

Suppose we have Gaussian distribution for the quantities x and y:

$$dW(x, y) = Ae^{-(ax^2+2bxy+cy^2)}\, dx\, dy \quad (-\infty < x, y < \infty). \tag{XIV.6}$$

The normalization integral for this expression can readily be evaluated, if the perfect square $ax^2 + 2bxy + cy^2 = a\left(x + \frac{by}{a}\right)^2 + \left(c - \frac{b^2}{a}\right)y^2$ is singled out from the exponent and integration in Eq. (XIV.6) is carried out first over x and then over y. The necessary and sufficient condition for convergence of the integral is the fulfilment of the inequality $ac > b^2$, and if this is so, then

$$J = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(ax^2+2bxy+cy^2)}\, dx\, dy = \frac{\pi}{\sqrt{ac-b^2}}, \tag{XIV.7}$$

$$A = \frac{\sqrt{ac-b^2}}{\pi}, \tag{XIV.8}$$

$$dW(x, y) = \frac{\sqrt{ac-b^2}}{\pi}\, e^{-(ax^2+2bxy+cy^2)}\, dx\, dy. \tag{XIV.9}$$

To find the mean values $\overline{x^2}$, $\overline{y^2}$ and correlation $\overline{xy}$, we differentiate formula (XIV.7) with respect to a, c and b respectively and find

$$\overline{x^2} = -\frac{\partial}{\partial a}(\ln J) = \frac{c}{2(ac-b^2)}, \tag{XIV.10}$$

$$\overline{y^2} = -\frac{\partial}{\partial c}(\ln J) = \frac{a}{2(ac-b^2)}, \tag{XIV.11}$$

$$\overline{xy} = -\frac{1}{2}\frac{\partial}{\partial b}(\ln J) = -\frac{b}{2(ac-b^2)}. \tag{XIV.12}$$

It follows from formula (XIV.12) that x and y are statistically independent ($\overline{xy} = 0$) when and only when the coefficient b equals zero.

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TO THE READER

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